

INFORMAL REPORT

CHEMICAL AND MECHANICAL FAILURE MODE DATA
REQUIREMENTS FOR BOROSILICATE GLASS WASTE FORMS

DRAFT REPORT

J. SHAO AND H. JAIN

MANUSCRIPT COMPLETED AUGUST 1982

NUCLEAR WASTE MANAGEMENT DIVISION
DEPARTMENT OF NUCLEAR ENERGY BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973



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ABSTRACT

A borosilicate waste glass alone cannot be credited with any radionuclide containment capability due to the immediate leaching of radionuclides from the glass upon contact with groundwater. However, the Type 304L stainless steel mold in which the glass is directly emplaced, and which may be considered to be a part of the waste form can provide some period of containment. A conceptual design in which a sacrificial nonradioactive glass layer encapsulates a waste glass may be considered for containment purposes. The various chemical and mechanical failure modes under salt and basalt repository conditions of a sacrificial glass layer and Type 304L stainless steel have been evaluated. The additional data required to characterize the chemical and mechanical behavior of the borosilicate waste form for waste package licensing are discussed and outlined.

CONTENTS

ABSTRACT	iii
FIGURES	vii
TABLES	ix
ACKNOWLEDGMENTS	xi
1. INTRODUCTION	1
2. CHEMICAL FAILURE MODES OF SACRIFICIAL GLASS LAYERS	2
2.1 Corrosion Mechanisms	2
2.2 Time Dependence of Leach Rates	3
2.3 Factors Affecting Glass Corrosion	4
2.3.1 Leach Solution Characteristics	4
2.3.2 Glass Characteristics	5
2.3.3 System Characteristics	7
2.4 Summary and Conclusions	8
2.5 References	8
3. MECHANICAL FAILURE MODES OF SACRIFICIAL GLASS LAYERS	11
3.1 Thermal Fracturing	11
3.2 Radiation Effects on Mechanical Properties	14
3.3 Static Fatigue and Delayed Failure	16
3.4 Additional Data Requirements for Characterization of Sacrificial Glass Mechanical Failure Modes	21
3.5 Summary and Conclusions	22
3.6 References	23
4. CHEMICAL FAILURE MODES OF TYPE 304L Stainless Steel	25
4.1 Uniform Corrosion	25
4.2 Pitting Corrosion	27
4.3 Crevice Corrosion	27
4.4 Galvanic Corrosion	30
4.5 Stress Corrosion Cracking	30
4.6 Hydrogen Embrittlement	34
4.7 Additional Data Required to Characterize Type 304L Stainless Steel Chemical Failure Modes	34
4.8 Summary and Conclusions	36
4.9 References	37
5. MECHANICAL FAILURE MODES OF TYPE 304L STAINLESS STEEL	40

5.1	Residual Stresses.	40
5.2	Radiation Induced Stresses	40
5.3	Lithostatic and Hydrostatic Pressures.	40
5.4	Additional Data Requirements for Characterization of Type 304L-SS Mechanical Failure Modes.	42
5.5	Summary and Conclusions.	42
5.6	References	42

FIGURES

2.1	Schematic Diagram of the Hydrated Layers on the Surface of an Alkali-Silicate Glass.	3
2.2	Effect of pH on Leaching of Commercial Container Glass	5
2.3	Effects of Components of a PNL Glass on Soxhlet Leach Rate	6
3.1	Sixty-Centimeter-Diameter Cross Section of (CM) Canister Number 200, 100 cm from bottom	12
3.2	Partial Section of (ICM) Canister ICM-7 (60-cm dia.), 60 cm From Bottom.	13
3.3	Effect of Heat Content and Cooling Conditions on Glass Stress.	15
3.4	Density Changes in ²²⁴ Cm-Doped Waste Glasses	18
3.5	Microstructure of the Waste Glass (PNL 77-260) Before and After Microfracturing.	19
3.6	Universal Fatigue Curve for Soda-Lime-Silicate Glasses	20
4.1	Effect of Temperature on the Pitting Potential of Various Stainless Steels in a 3% NaCl Solution	28
4.2	Effect of pH on the Pitting Potential of Various Stainless Steels in a 3% NaCl Solution	28
4.3	Probability of Crevice Corrosion Initiation as a Function of Bold/Crevice Area Ratio	29
4.4	Effect of Chloride Concentration on the Cracking Susceptibility of Type 304 Stainless Steel Exposed at 100°C Under the Concentrating Conditions of the Wick Test.	31
4.5	Relationship Between Chloride and Oxygen Content of Alkaline-Phosphate Treated Boiler Water and Susceptibility to stress Corrosion of Austenitic Stainless Steel Exposed to the Steam Phase With Intermittent Wetting.	32
4.6	Effect of Temperature on the Chloride Cracking Resistance of Type 304 and 347 Stainless Steels in 0.1-33.0% Sodium Chloride Solution Containing Oxygen	33

4.7	Ductility (Elongation) of Type 304L-SS Sheet Specimens After the Exposures Shown	35
5.1	Reference DHLW Package for Borehole Emplacement in Salt	41

TABLES

3.1	Composition of PNL Simulated High Level Waste Glasses.	17
3.2	Abrasion Methods Used by Mould and Southwick	19
4.1	PNL Brine Solution Composition	26
4.2	Synthetic Hanford Groundwater Formulations	26
4.3	Effect of Seawater Temperature on the Probability of Crevice Corrosion Initiation	30

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1. INTRODUCTION

The definition and functions of a high level waste package have been outlined in proposed Nuclear Regulatory Commission (NRC) 10 CFR 60 performance criteria. A primary function of the waste package is the containment of all radionuclides for approximately the first 1000 years after closure of the geologic repository. The waste form is the innermost barrier against radionuclide release. Currently, the major waste form research and development efforts are centered on borosilicate glass.

Since borosilicate glasses have finite leach rates, they cannot alone meet the 1000-year containment criterion. An alternative waste form which incorporates a sacrificial layer of nonradioactive glass over a radioactive borosilicate glass core could conceptually meet containment requirements. In a current design, Type 304L stainless steel functions as the mold in which the waste glass is solidified. If this metal layer can prevent groundwater or brine penetration to the radioactive waste glass for a period of time, then this component of the waste form has containment capability.

A range of chemical and mechanical failure modes could cause a loss in the integrity of these waste form components. This report will briefly review and outline the available data relevant to the various failure modes of a sacrificial glass layer and Type 304L stainless steel mold under repository conditions. The additional data required for licensing will then be specified.

2. CHEMICAL FAILURE MODES OF SACRIFICIAL GLASS LAYERS

The most important consideration for a given waste form is its capability to retain radionuclides upon contact with groundwater. In recent years, significant efforts have been directed towards obtaining data on the chemical durability of borosilicate glass containing high level waste. Leaching of radionuclides from these glasses begins immediately upon contact with water. Therefore, no credit for containment can be given to this type of waste form.

To inhibit immediate release of radionuclides, Simmons and others¹ have suggested the use of a thin sacrificial layer of nonradioactive glass. They used a "Porous Glass Matrix" to incorporate radionuclides in a high silica glass which is then contained in a nonradioactive glass tube. By heating to high temperatures this tube collapses and forms a cladding around the waste glass. It has been suggested that the stresses developed during this cladding procedure will improve the properties of this waste form. The so-called sacrificial layer may provide sufficient leach resistance to meet the NRC specification, but the technical problems in producing full scale cladded borosilicate glass waste forms under realistic conditions have not been addressed. At this time, basic design information, such as the composition of cladding glass, etc., have not been established. Therefore, without restrictions to any specifications of the sacrificial layer or the technology² to develop it, this report addresses the general problems of glass corrosion expected in a repository. Various parameters which may affect the corrosion life of the sacrificial layer, have been identified. Data will be needed as a function of these variables.

A common problem in evaluating the corrosion resistance of a glass is the lack of a unique parameter to describe it. Much of the available data concerns the leach rates of different elements. From this information, it is not clear when a sacrificial layer will stop functioning as a barrier to the release of radionuclides; it will obviously become ineffective if the glass matrix is completely dissolved. Mendel and others³ have discussed the expressions for chemical durability and found "normalized leach rates" to be the quantity most often calculated to represent the overall leach resistance.

2.1 Corrosion Mechanisms

Recently, several good reviews describing the reaction of glass with water have appeared in the literature.⁴⁻⁷ Usually a discussion of glass durability centers around silicate glasses containing some network modifiers, particularly the alkali ions. Nevertheless, similar ideas can be extended to more complicated glass compositions. Details of these mechanisms are not well understood, and may depend on the properties of the glass or the leachant. Therefore, only a brief overview of the understanding of leaching behavior is presented below.

There are two main stages in the leaching of glass in water. Initially, preferential out-diffusion of alkali cations occurs, leaving behind silica-rich layers. With time, the silica-rich layer becomes thicker and the diffusion of alkali ions through it, progressively slower. Eventually, the rate of

release is determined by the dissolution of the silica-rich layer itself. At this stage, the glass dissolves congruently, i.e., the elements leach in the same proportion as they are present in the glass. Thus, the durability of a glass depends on the structure of this layer and improves with increasing silica content.⁸ The dealcalized silica-rich layer may incorporate some hydroxyl bonds during the alkali-hydronium ion interdiffusion process, thus giving it a gel-like structure (shown schematically in Figure 2.1). When the mole fraction of silica drops below a specific value (approximately 2/3) such that a continuous Si-O network cannot be maintained, the chemical durability of the glass falls sharply.

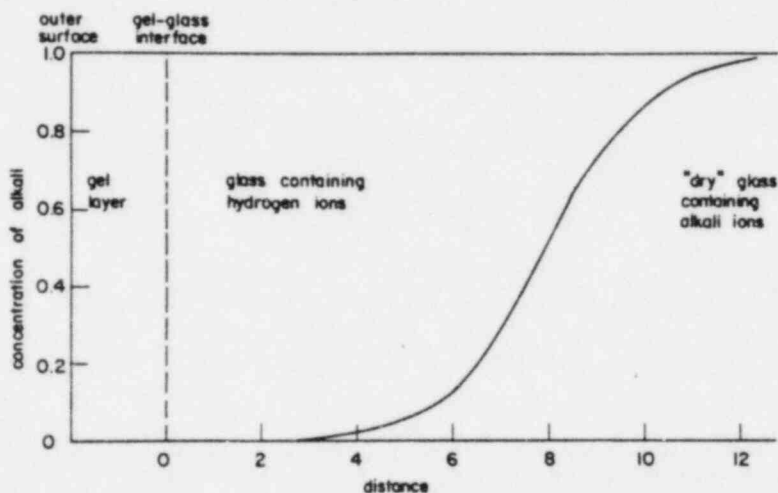


Figure 2.1 Schematic diagram of the hydrated layers on the surface of an alkali-silicate glass.⁴

Barkatt and others⁵ have noticed that polyvalent ions from a waste glass can be trapped within the dealcalized protective layer. This effect can continue until the surface layer becomes saturated. At this point, the leach rate of these ions will increase sharply.

2.2 Time Dependence of Leach Rates

To evaluate the long term durability of a glass, it is important to be able to extrapolate laboratory data to the repository time scale. As described above, the first stage of leaching is usually diffusion controlled, which implies a square root dependence on time t . Subsequent dissolution is interface controlled and should have a linear time dependence. Thus, the amount of glass leached can be expressed as:⁹

$$Q = a \sqrt{t} + bt$$

where a and b are constants. The leach rate can then be written as:

$$\frac{dQ}{dt} = \frac{a}{2} t^{-1/2} + b .$$

Using the above expression, Lanza and Panisari¹⁰ have analyzed their data on the leaching for 8000 hours of borosilicate glass. They found that only the tests above 80°C could give useful results for the purpose of extrapolation. Other experiments have shown more complex behavior with a t^{-1} power law.¹¹

There are several factors which might make the use of simple equations such as those mentioned above invalid. Due to the absorption of polyvalent ions in the dealcalized layer, the leach rate may increase considerably. Further, it is known that during ion-exchange between the alkali and hydronium ions enough stresses can develop in the surface layer to cause cracking or peeling. This will increase the leach rate and may result in a cyclic leaching pattern.¹² Any crystallization occurring in the surface layer can also complicate the corrosion process. As leaching continues, the properties of the solution such as composition, pH, Eh, etc. may change and thereby affect the corrosion kinetics. In short, to be able to extrapolate laboratory data to much longer time periods, it must be shown that the leaching mechanisms and conditions will not change significantly.

2.3 Factors Affecting Glass Corrosion

Corrosion of a waste glass is a very complex process and is dependent upon several interdependent variables.^{6,13} Various factors contributing to this phenomenon may be divided into three major categories depending upon their relation to the properties of solution, glass, or the system as a whole. These are briefly discussed below.

2.3.1 Leach Solution Characteristics

- Composition

Brine as well as basaltic groundwater can contain substantial amounts of alkalis, divalent cations, and various anions including H_3SiO_4 .¹⁴ These chemical species can affect the leaching properties of glass through solubility saturation effects or by altering the properties of the surface layers. For example, the leach rates of glass have been found^{15,16} to be successively lower in de-ionized water, groundwater, and brine. However, Johnson and Marples¹⁷ have not found any difference between the leaching of borosilicate glass in distilled water and in seawater.

- pH of the Solution

The pH of solution can have a strong effect on the durability of a glass. In acidic and neutral solutions primarily the alkalis and other element additions are leached, but in alkaline environments, the silica network can also begin to dissolve. A typical pH dependence of the rate of attack on glass is shown in Figure 2.2.¹⁸ In borosilicate glasses, the attack at low pH can be much stronger.

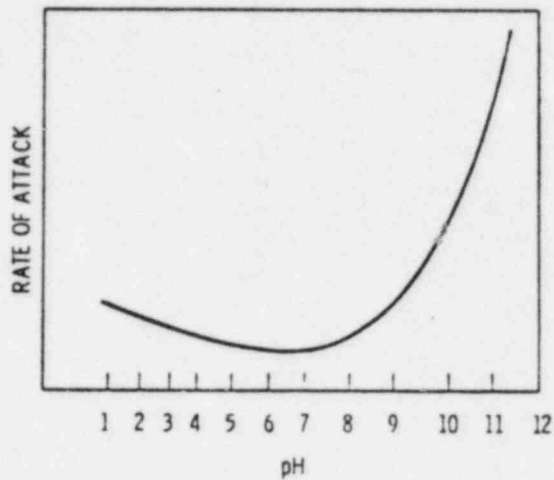


Figure 2.2 Effect of pH on leaching of commercial container glass.¹⁸

- Flow Rate

Macedo and others¹⁹ have considered in detail the effect of flow rate or replenishing frequency of corrosion solution in a leach test. At low to moderate flow rates, the alkalis dissolving out of the glass will increase the solution pH and hence the leach rate. On the other hand, at very high flow rates the leached ions will be continuously removed from the glass surface. This will eliminate any contribution to leach resistance from concentration effects and, therefore, may also result in an increased leach rate. Thus, the effect of flow rate on the stability of glass is rather complex and is indirectly determined by the glass composition as well.

2.3.2 Glass Characteristics

- Composition

The amount of network forming oxides (particularly silica) relative to the amount of network modifiers is perhaps the most important factor in determining the properties of a glass. In general, increasing the proportion of silica increases the durability of a glass. Small additions of ZrO_2 and Al_2O_3 are known to increase the chemical durability in a wider pH range. Based on a PNL study,²⁰ the effects of various components may be predicted as shown in Figure 2.3. Note that the addition of B_2O_3 does not follow a systematic pattern. Finally, a compromise in glass composition may be necessary to optimize the chemical durability along with the thermal expansion coefficient and glass melting temperature.

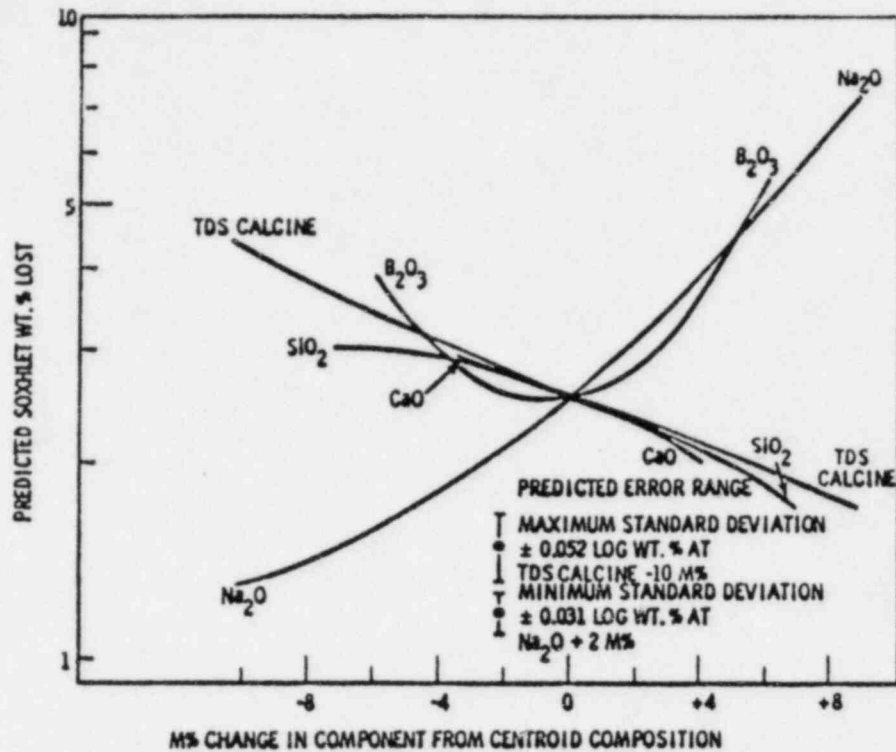


Figure 2.3 Effects of components of a PNL glass on Soxhlet leach rate.²⁰

- Phase Separation

Many glasses (e.g., alkali silicates, borosilicates, etc.) separate into two or more phases.²¹ In those cases, the glass phase lower in silica content may leach at a faster rate than the rest of the glass. Thus, the phase separation of a glass may lead to an overall decrease in its durability. The extent of phase separation strongly depends on the composition of the glass as well as any heat treatment given to the glass. For some compositions, the glass may phase separate in the process of manufacturing itself.

- Devitrification

Under the proper conditions of time and temperature, a glass will change into a crystalline form. The effect of this devitrification on corrosion depends on the glass composition and the degree of devitrification. In many cases, the formed grain and phase boundaries can decrease the durability of the glass ceramic.⁶

- Surface Conditions

Surface roughness can play an important role in the corrosion of glass. Increasing roughness will increase the effective exposed

surface area and hence also the corrosion rate. An increase in local pH within the surface scratches can lead to higher silicon dissolution. The effect of roughness on selective leaching is largely composition dependent.²² A simple model for this mechanism has been recently proposed by Pescatore and Machiels.²³ Thermal stresses, devitrification, etc. can easily cause the fracture of glass and produce cracks. The effect of cracking on chemical durability is briefly discussed in other sections of this report.

- Glass Surface Area to Solution Volume Ratio

In general, following the arguments given for the effect of solution flow rate, one may expect an increase in corrosion rate when the surface area to solution volume ratio (SA/V) is increased. However, a borosilicate glass exhibited selective leaching at low SA/V values and congruent dissolution at high ratios.²² The net effect was a decrease in overall corrosion rate. Therefore, data will be needed to quantify this effect under realistic conditions.

2.3.3 Systems Characteristics

- Temperature

The chemical durability of a glass falls rapidly with increasing temperature. Often, leach rates are characterized by Arrhenius type behavior in a limited temperature range. At high temperatures, the dissolution rate may increase rapidly due to hydrothermal effects and a single activation energy may not be appropriate.²⁴ A temperature dependence of the surface film properties further complicates the problem. Occasionally, due to solubility effects, leaching of certain elements in a glass may show an inverse temperature dependence.²⁵

- Radiation

The surface layer of sacrificial glass will be irradiated by gamma rays generated from the nuclear waste. Most of the available information^{3,26} indicate that the leach rate of γ -irradiated glass is about the same as that of unirradiated glass. However, the radiolysis products, such as nitric acid, can cause enhancement in glass corrosion.²⁶

- Weathering

An exposed glass surface can react with water vapor present in the environment. The extent of this attack increases with humidity and temperature. Bates and others²⁷ have found that leaching from a hydrated layer formed by weathering can be higher than from an unexposed glass by a factor of 1000. Cyclic humidity and intermittent removal of a weathered layer can increase the total corrosion rate substantially. Usually, weathering is increased by the presence of alkali ions in the glass and reduced by Zn, Sr, Ba, Pb, Zr, etc.

• Other Characteristics

Some enhancement in corrosion may occur due to interactions among the factors mentioned above. Impurities from the leaching solution or from the backfill can modify the surface layer and other corrosion characteristics. Finally, pressure is not likely to be an important factor for glass corrosion; e.g., no significant adverse effect of pressure (up to 1500 psi) was found on the chemical durability of a simulated waste glass.²⁸

2.4 Summary and Conclusions

For a borosilicate waste glass to have containment capability under repository conditions, a sacrificial layer of nonradioactive glass will be needed. The design of this clad glass remains to be developed and manufacturing related problems remain to be solved. Experimental data will then be needed to evaluate the corrosion resistance of the sacrificial layer. Of course the corrosion life of the cladding can be improved by increasing its thickness, unless this leads to poorer mechanical stability due to internal stresses, etc.

Assuming that the composition of sacrificial glass has been decided, the corrosion data will be needed primarily as a function of the following variables:

1. pH, composition, and flow rate of the repository water
2. Temperature
3. Changes in repository water due to irradiation
4. Glass surface conditions: roughness, surface area to solution volume ratio, and any weathering of the surface due to humidity
5. Devitrification and phase separation for certain glass compositions.

Irradiation of the glass and pressure are expected to be of minor importance in terms of effects on the corrosion rate. Finally, long term testing data should be obtained so that reliable extrapolation can be made to repository times.

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3. MECHANICAL FAILURE MODES OF SACRIFICIAL GLASS LAYERS

At present, a borosilicate glass waste form with a sacrificial glass layer is only a conceptual design. Its fabrication may be difficult and perhaps not even feasible (due to technical problems and cost). Macedo and others¹ have developed a process (porous glass matrix method) in which a high silica glass tube is collapsed around a waste glass core. Mechanical strengthening and good resistance to stress corrosion of the glass is a result of high residual compressive stresses on the surface. Further studies would be required in the application of such methods to the full scale production of large waste forms.

The mechanical failure modes addressed here are those which can cause fracturing and cracking of the sacrificial glass. There is much controversy on the effects of cracking on glass leaching. A Pacific Northwest Laboratory (PNL) study of partially devitrified ²⁴⁴Cm-doped waste borosilicate glass exhibited microfracturing with no accompanying measurable effect on leach rate.² Perez and Westik³ simulated cracks by stacking glass pellets with platinum wire spacers and clamping them together. Their findings indicated that crack depth and crack width are important parameters with the possibility of a minimum width limit required to enhance leaching.

In terms of a sacrificial glass layer, the leaching of the radioactive glass core and radionuclide transport through a fractured sacrificial layer would be of prime importance.

3.1 Thermal Fracturing

There are two processes currently being considered for solidifying wastes in borosilicate glass. The continuous melting (CM) process involves filling "canisters" with molten glass produced in a continuously operating furnace. The in-can melting (ICM) process is a batch operation in which waste glass is formed in a mold with externally supplied heat. Though the fabrication process will differ for a waste glass with a sacrificial layer, the information regarding thermally induced cracking is still relevant.

The causes of cracking in waste-filled canisters have been investigated and discussed by Slate and others^{4,5} (see Figures 3.1 and 3.2). Fracturing can occur from either thermal gradients or the bonding coupled with thermal expansion mismatch at the glass/metal interface. In the former case, the extent of cracking increases with the magnitude of the temperature gradients. These gradients are established during casting when the glass is soft and non-brittle. Fracturing occurs when the glass cools and reverse strains develop.⁶ The studies by Slate and others suggest that this form of cracking can be eliminated by proper cooling processes. However, it becomes a complex problem as cooling times required are estimated to be about three weeks. With a large inventory of canisters this would require a costly system of furnaces.

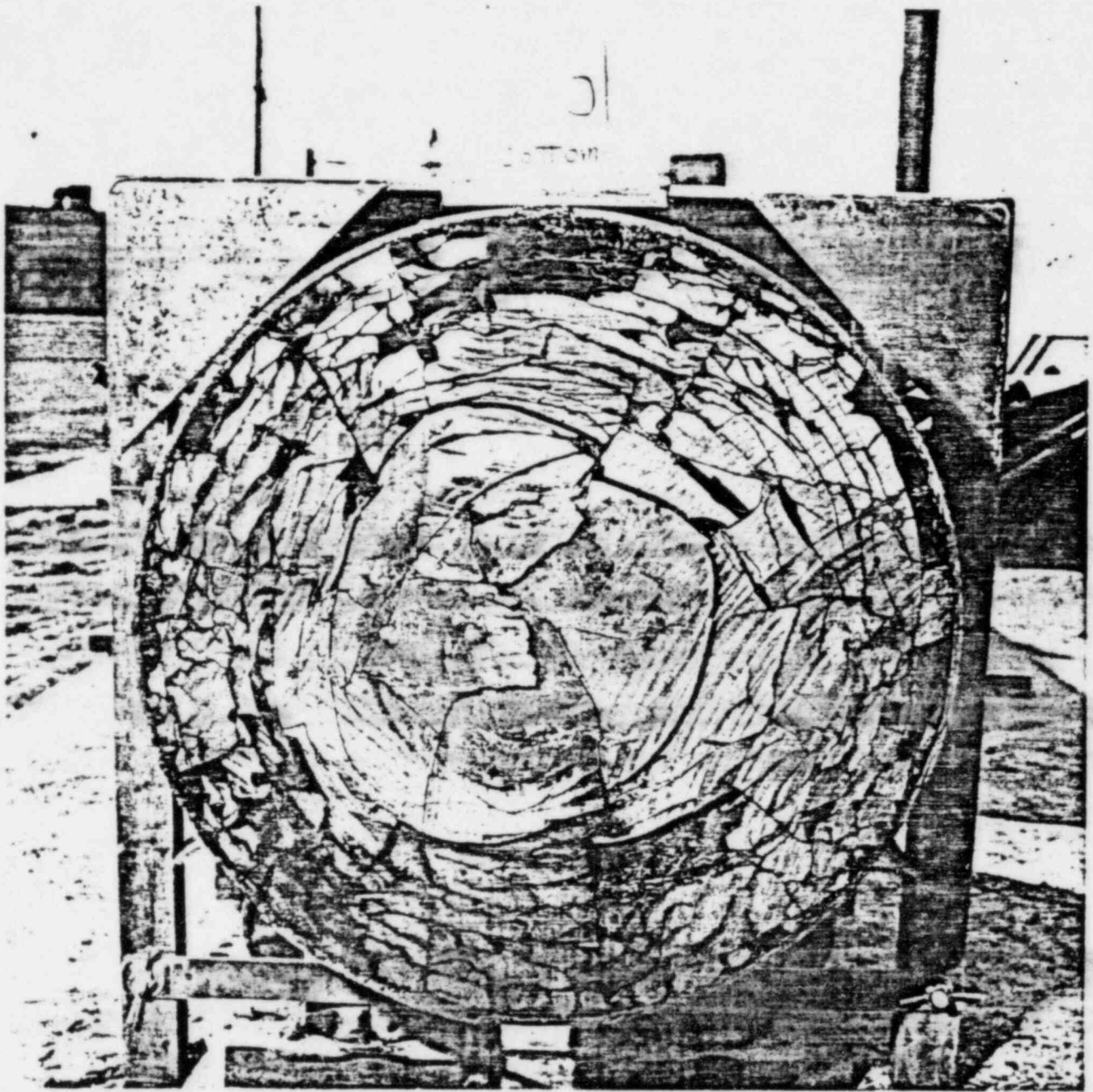


Figure 3.1 Sixty-centimeter-diameter cross section of (CM) canister number 200, 100 cm from bottom.⁵



Figure 3.2 Partial section of (ICM) canister ICM-7 (60-cm dia.),
60 cm from bottom.⁵

During cooldown, the difference in thermal expansion coefficient resulted in large shear forces due to the resistance to movement of the metallic mold relative to the glass. The expansion coefficient of Type 304L stainless steel is $1.7 \times 10^{-5}/^{\circ}\text{C}$ which is about twice as large as that for borosilicate glass. This type of fracture is largely independent of temperature gradients and thus cooling rates. Shear fracture was determined to be the cause of cracking in the outer 2 cm of glass in ICM canisters (60-cm diameter). It was suggested that this effect could be reduced or eliminated with a graphite coating applied to the inside of the stainless steel mold.⁵

Cracking can also occur during the filling of CM canisters due to thermal shock from the mold wall and thermal gradients from uneven filling. Uneven filling causes irregular temperature gradients in the main body of the glass, so the resulting cracks are hard to evaluate. However, the gradients are small, so little cracking is expected. Contact with cold mold walls causes thermal shock and severe localized cracking. It has been suggested that preheating the mold to the glass transition temperature would substantially reduce this localized cracking.⁴

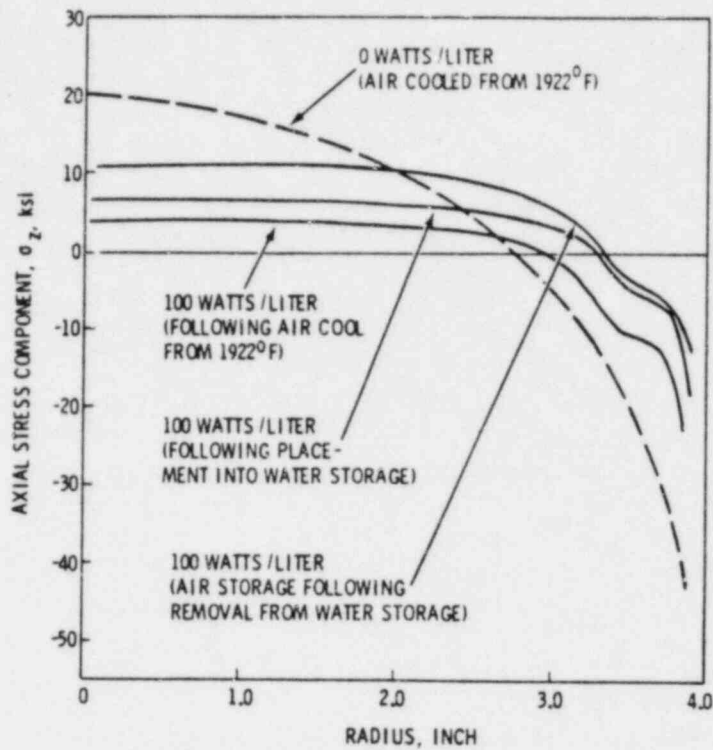
Simonen and Friley⁷ used finite element computer calculations to simulate residual stresses and cracking in canisters filled with vitrified nuclear waste (ICM process). Figure 3.3 shows predictive stress levels in the glass for various cooling conditions. Differences between non-self-heating glass and a high heat content glass of 100 watts/liter are shown. For cooling rates typical of proposed vitrification processes, glass stresses well in excess of typical glass strengths (about 38 MPa or 5.5 ksi)⁴ were predicted indicating that cracking will occur.

The study showed that in response to radioactive decay, glass stress increases as the heat generation rate in the glass decreases. The analyses suggest that radioactive glass with high heat rates will be less extensively cracked initially but may, over long time periods, continue to crack in response to a decaying heat rate.⁷

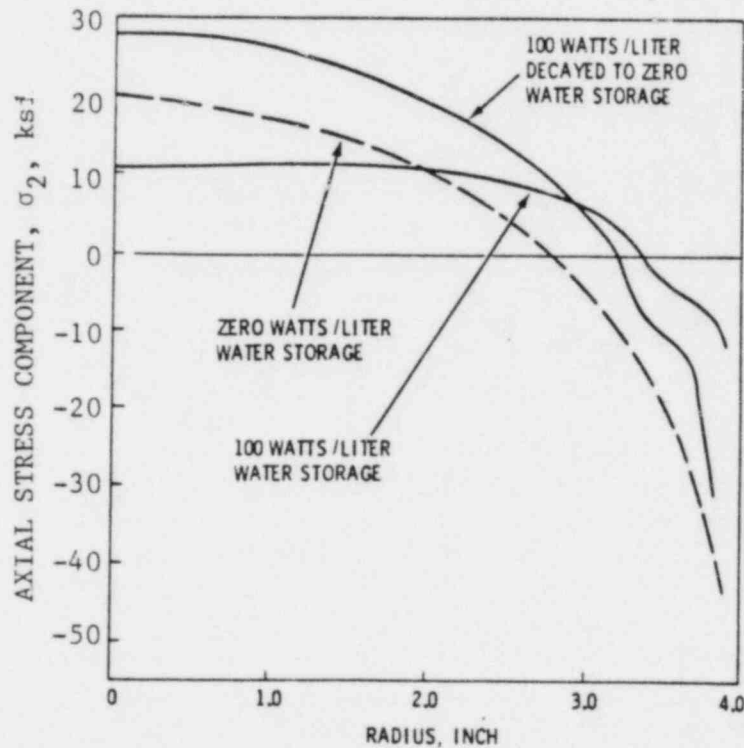
3.2 Radiation Effects on Mechanical Properties

The solidified high level radioactive waste forms will receive massive doses of self irradiation during their projected service lives. The radioactive waste glass will be subjected to neutron, gamma, beta, and alpha radiation and possibly heavy ion bombardment, whereas, the sacrificial glass layer should be exposed mainly to gamma doses (except near the radioactive glass interface).

The thermal stress cracking caused by a decaying self-heating rate has been discussed in the previous section. Irradiation at the levels anticipated in HLW forms is also known to cause changes in density, strength, thermal conductivity, and lattice structure.^{8,9} Glassy waste forms are usually microstructurally inhomogeneous, often partially devitrified with dispersed small size (1 to 1000 μm) crystalline phases. The radionuclides may be inhomogeneously distributed within the waste form, resulting in an inhomogeneous



(a) EFFECT OF HEAT CONTENT ON GLASS STRESS



(b) CHANGE IN GLASS STRESS AS HEAT CONTENT OF GLASS DECREASES DURING PERIOD OF STORAGE

Figure 3.3 Effect of heat content and cooling conditions on glass stress.⁷

radiation dose. Under these conditions, microcracking may occur due to differential stresses arising at interfaces or grain boundaries from nonuniform swelling or compaction in different phases.

Waste glasses can either expand or compact under irradiation^{9,10} (see Table 3.1 and Figure 3.4). The density changes were a function of glass composition, accumulated dose, and heat treatments. The results indicate that volumetric changes in these waste glasses can reach approximately +1% which can lead to internal stresses and possible strains in the metal mold.

Weber and others¹¹ performed impact tests on a vitreous (~2 weight percent crystalline) and two partially devitrified (~30 weight percent crystalline) forms of ²⁴⁴Cm-doped PNL 77-260 waste glass. It was concluded that the impact performance was not adversely affected by the self-radiation. Extensive microcracking was observed, however, in one of the partially devitrified forms of these glass compositions which contained large crystals (~25 to 1000 μm in size) from a slow cool of 6°C/hr from 1050°C (see Figure 3.5). The fracturing was associated with the amorphization of the crystalline devitrification product Ca₃Gd₇(SiO₄)₅(PO₄)O₂. No microcracking was observed in the other partially devitrified glass containing smaller crystals (<5 μm in size from an anneal at 700°C for one week), even though the same phase was present and also underwent amorphization. However, after immersion in room temperature water for three weeks, this same partially devitrified glass also experienced cracking. Identically prepared, but undoped, samples were also exposed to water. No effects were observed, confirming that the observed microfracturing was a result of radiation induced stresses.

3.3 Static Fatigue and Delayed Failure

Glass is extremely susceptible to stress corrosion cracking caused by water in the environment. In this phenomenon, also known as static fatigue, the presence of small quantities of water is sufficient to cause a substantial reduction of the strength of a glass. Although glass can withstand a given stress for a short period of time, lower stresses can lead to fracture if applied for a sufficiently long period of time. Experimental investigations have shown that the static fatigue results from surface cracks that grow when glass is subjected to tensile loads.¹²

Mould and Southwick¹³ studied the delayed failure of soda-lime silica glass. They used different methods of abrading the glass surface to give different degrees of damage (see Table 3.2). They found that all the data could be fit onto a single universal fatigue curve by dividing the room temperature strength values for each abrasion treatment by the low temperature strength for that treatment and plotting the resulting values against a reduced time coordinate. Such a curve is shown in Figure 3.6 which indicates a long term strength equal to approximately 20% of the short term or low-temperature strength. Other glasses of different compositions are characterized by different universal fatigue curves.

Table 3.1

Composition of PNL Simulated High Level Waste Glasses⁹

Component	Weight Percent of Component					
	72-68a	72-68b	76-68	76-260	E-G	P-G
Glass						
Components:						
SiO ₂	27.0	27.0	38.8	34.9	50.6	23.4
B ₂ O ₃	11.0	11.0	9.2	8.7	12.7	7.3
Li ₂ O	—	—	—	—	4.0	—
Na ₂ O	4.0	4.0	7.3	7.8	5.1	2.8
K ₂ O	8.0	4.0	—	1.9	—	2.8
TiO ₂	—	—	2.9	5.8	—	—
CaO	1.5	1.5	1.9	1.0	2.6	—
MgO	1.5	1.5	—	—	—	—
SrO	1.5	1.5	—	—	—	—
BaO	1.5	1.5	—	—	—	—
Al ₂ O ₃	—	—	—	1.9	—	—
ZnO	21.0	21.0	4.9	—	—	—
PbO	—	—	—	—	—	38.0
CuO	—	—	—	2.9	—	—
Fission						
Products:						
Rb ₂ O	0.22	0.22	0.12	0.10	0.22	0.22
SrO	0.65	0.65	0.36	0.26	0.65	0.65
Y ₂ O ₃	0.02	0.02	0.20	0.15	0.02	0.02
ZrO ₂	3.04	3.04	1.70	1.33	3.04	3.04
MoO ₃	3.91	3.91	2.17	1.73	3.91	3.91
RuO ₂	1.82	1.82	1.02	0.76	1.82	1.82
Rh ₂ O ₃	0.30	0.30	0.17	0.14	0.30	0.30
PdO	0.91	0.91	0.51	0.44	0.91	0.91
Ag ₂ O	0.05	0.05	0.03	0.02	0.05	0.05
CdO	0.05	0.05	0.03	0.03	0.05	0.05
TeO ₂	0.45	0.45	0.25	0.19	0.45	0.45
Cs ₂ O	1.77	1.77	0.99	0.07	1.77	1.77
BaO	0.96	0.96	0.54	0.49	0.96	0.96
La ₂ O ₃	1.97	—	0.51	0.40	1.97	1.97
CeO ₂	3.98	—	1.15	0.81	3.95	3.95
Pr ₆ O ₁₁	0.41	—	0.51	0.39	0.41	0.41
Nd ₂ O ₃	1.40	—	1.60	4.13	1.40	1.40
Sm ₂ O ₃	0.25	—	0.32	0.01	0.25	0.25
Eu ₂ O ₃	0.06	—	0.07	0.05	0.06	0.06
Gd ₂ O ₃	0.17	—	0.05	0.03	0.17	0.17
Actinides:						
U ₃ O ₈	—	—	4.39	4.67	—	—
Cm ₂ O ₃	1.0	8.2	3.0	3.0	1.0	1.0
Others:^a						
Na ₂ O	—	—	4.84	2.81	—	—
Fe ₂ O ₃	0.93	0.93	9.38	1.08	0.3	0.93
Cr ₂ O ₃	0.21	0.21	0.40	0.02	0.21	0.21
NiO	0.09	0.09	0.20	0.01	0.09	0.09
P ₂ O ₅	0.41	0.41	0.46	2.08	0.41	0.41
MnO ₂	—	—	—	0.09	—	—
Gd ₂ O ₃	—	—	—	9.11	—	—
ZrO ₂	—	—	—	0.12	—	—

^aIncludes corrosion products, nuclear poisons, process chemicals, and cladding residues.

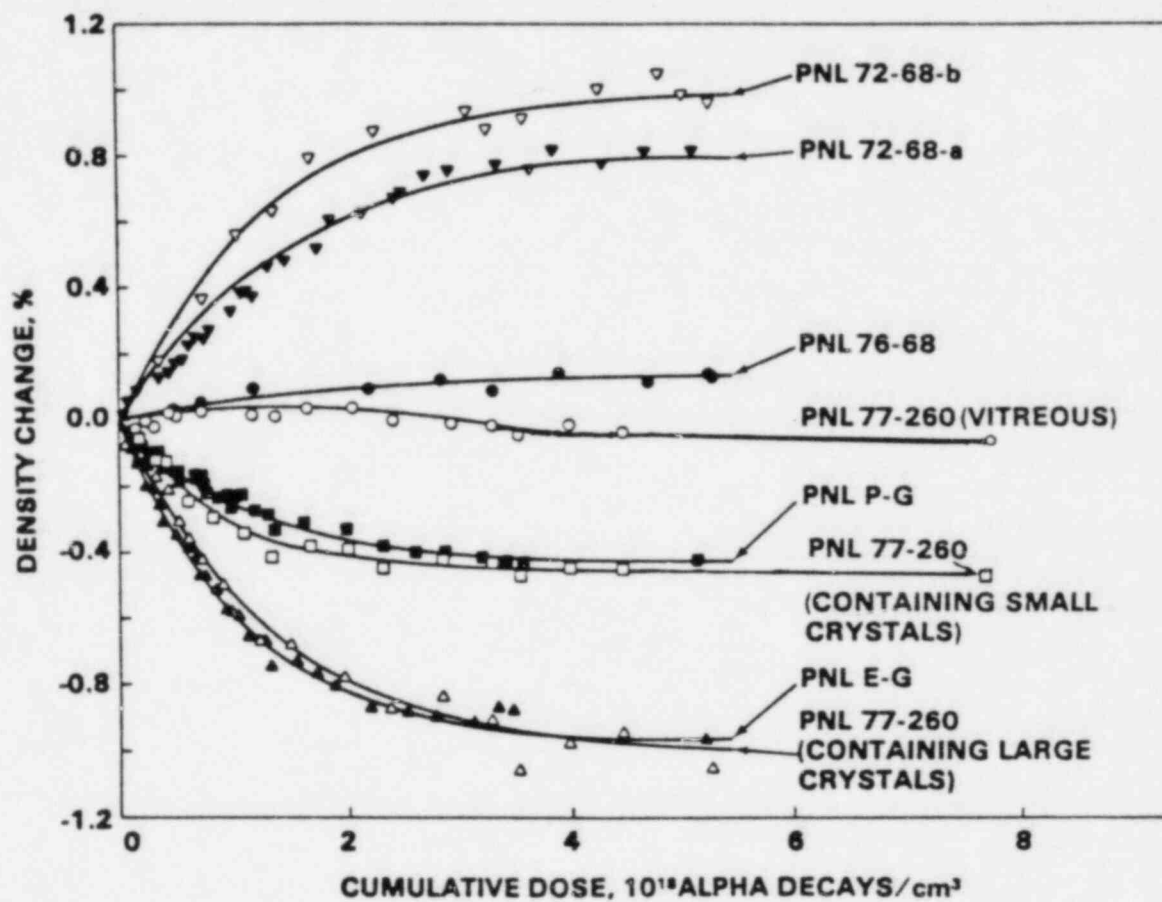


Figure 3.4 Density changes in ²²⁴Cm-doped waste glasses.^{9,10}

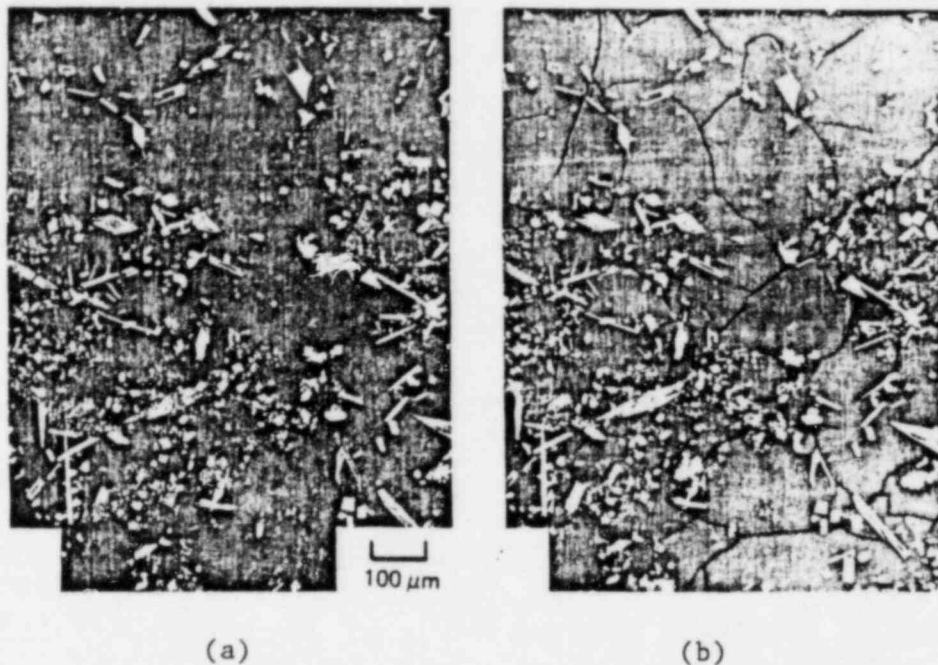


Figure 3.5 Microstructure of the waste glass (PNL 77-260) before and after microfracturing: (a) slow cooled samples exhibiting no microcracks after 2×10^{16} α decays/cm³; (b) microcracks developed in same area after 8×10^{17} α decays/cm³.¹¹

Table 3.2

Abrasion Methods Used by Mould and Southwick¹³

Designation	Abrasion
a	Grit blast, severe
b	Grit blast, mild
c	Emery cloth, 150 grit parallel to stress
d	Emery cloth, 600 grit perpendicular to stress
e	Emery cloth, 320 grit perpendicular to stress
f	Emery cloth, 150 grit perpendicular to stress

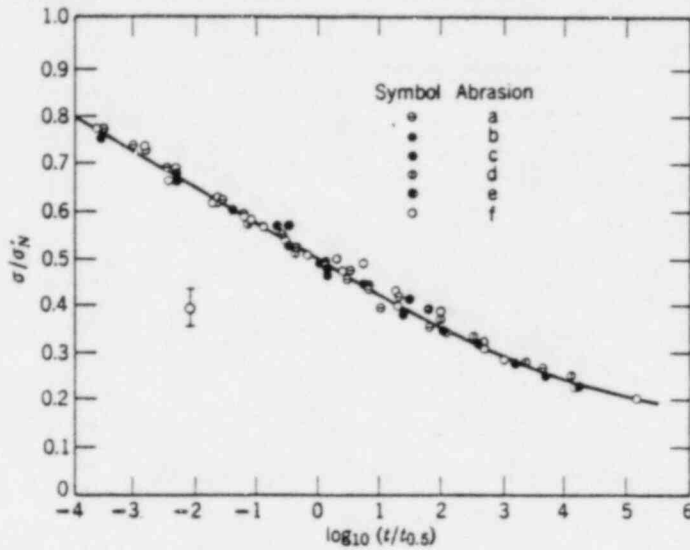


Figure 3.6 Universal fatigue curve for soda-lime-silicate glasses; σ is the room temperature strength; σ'_N is the strength at 77°K; $t_{0.5}$ is the time with a given abrasion treatment for the strength to fall to a half of its value at 77°K.^{13,14}

W. B. Hillig and R. J. Charles¹⁵ have developed a stress corrosion model to explain the universal fatigue curve. S. M. Wiederhorn¹⁶ successfully used it to describe his experiments in which crack velocity in soda-lime-silicate glasses were measured as a function of temperature, environment, and stress intensity factor. It was found that crack velocity v varies exponentially with the stress intensity factor K_I and can be described by the following empirical equation:

$$v = AK_I^n \quad (1)$$

where A is a constant and n is usually in the range of 30 to 40.¹⁷

S. M. Wiederhorn and L. H. Bolz¹⁸ used fracture mechanics techniques to obtain information on the activated processes during stress corrosion cracking. The data were found to fit the equation:

$$v = v_0 \exp [(-E^* + bK_I)/RT] \quad (2)$$

where v_0 , E^* , and b are empirically determined constants. For borosilicate glass in water the data yielded:^{18,19}

$$\begin{aligned} E^* &= 30.8 \text{ Kcal/mole} \\ b &= 0.200 \text{ (m}^{5/2}\text{/mole)} \\ \ln(v_0) &= 3.5. \end{aligned}$$

The application of fracture mechanics to glass has resulted in the development of proof testing as a method of predicting minimum times to failure as a function of service stress and proof test stress.²⁰ This technique involves the application of a proof test stress to the glass specimens. Those glasses which survive this stress should contain an upper limit to the size of the cracks present. Knowing this maximum crack size and the crack propagation velocity as a function of stress intensity factor for the material, a minimum service life under given stress conditions could be obtained.

Use of this approach depends on factors such as ensuring that:¹⁴

- Additional damage does not occur to the body during subsequent handling
- Conditions of the proof test approximate to the conditions of use
- In-service stress conditions for the bodies can be estimated
- Crack velocity vs K_I relations are available for similar stress conditions as expected during use.

The large uncertainties in the stresses and environmental conditions the sacrificial glass will encounter during the long term period of interest and the difficulties involved in the proof testing of actual waste forms will probably limit the use of this technique.

The static fatigue mechanism in glass is a complex stress corrosion process and therefore, the environmental variables which can affect glass corrosion will also affect delayed failure (see Section 2). These include the solution composition (i.e., chemical species, pH, Eh), humidity, temperature, microstructure, and glass composition. In general, decreased surface flaw sizes and/or stress levels will increase the time to failure.

3.4 Additional Data Requirements for Characterization of Sacrificial Glass Mechanical Failure Modes

Mechanical failure of a sacrificial borosilicate glass layer will occur under a variety of conditions. If fabrication techniques can be developed to manufacture waste forms with sacrificial glass, there still remains the problem of fracturing due to thermal, radiation, corrosion, and other effects.

The extent of fracturing due to thermal stresses can be reduced with proper waste package designs and procedures, e.g., matching thermal expansion coefficients of various components, preheating CM molds, lubrication, slow cooling, etc. However, little is known about the thermal stress effects caused by decaying self-heating rates and local temperature gradients caused by waste glass inhomogeneities.

Determining the effects of radiation is another complicating factor. The stress caused by density changes should be investigated to determine how they are affected by dose rates, waste glass/sacrificial glass/mold interactions, glass compositions, and time. Fracturing resulting from radiation induced amorphization should also be studied further. The severity of these problems

can also be mitigated to some degree through design, e.g., altering the glass composition, but this may not be a simple task.

It is impossible for all residual stresses, thermal stresses, and radiation induced stresses to be eliminated. There is also a high probability that mechanical flaws resulting from fabrication, radiation, or handling will exist. Static fatigue testing should be performed in basaltic waters and brines to characterize crack growth rates, time to failure relationships, temperature and radiation dose rate dependencies, and critical flaw sizes or static fatigue limits, if any. Proof testing or similar techniques may be useful in predicting time to failure, however, much further investigation would be required.

Quantitative data for borosilicate glass on cracking due to devitrification and hydration are lacking. Testing should be performed to study environmental interactions and long term effects.

3.5 Summary and Conclusions

The development of a sacrificial layer of borosilicate glass, which will remain mechanically stable under waste repository conditions for one thousand years, is a formidable task. This glass must be compatible with both the radioactive glass core and the external mold. Large stresses must be avoided from thermal (temperature gradients, unmatched thermal expansion coefficients, decaying self-heating rates, thermal shock), radiation (density changes, void and defect formation, amorphization, inhomogeneous dose rates), corrosion (static fatigue, hydration), and other (devitrification, phase separation) effects.

The additional data required to characterize the mechanical failure modes under waste repository conditions are as follows:

- Proper designs and procedures should be developed to minimize thermal stresses. This may include preheating of the mold, lubrication, various slow cooling schemes, etc.
- The compatibility between waste glass, sacrificial glass, and the mold should be assessed, e.g., thermal expansion coefficients and interface bonding strengths should be determined.
- Thermal stresses resulting from decaying self-heating rates should be investigated.
- Thermal stresses resulting from local temperature gradients caused by glass inhomogeneities should be investigated.
- Radiation induced density changes and resulting stresses should be characterized. This includes the effects of dose rates, glass compositions, and time.

- Cracking due to radiation amorphization has been observed. Further quantification of this phenomenon is required.
- Static fatigue testing of the glass should be performed in basaltic waters and brines. Crack growth rates, time to failure relationships, temperature and radiation dose dependences, and critical flaw sizes or static fatigue limits, if any, should be determined.
- Proof testing of the glass may be a useful technique for predicting times to failure, however, much further investigation would be required.
- Devitrification and hydration effects require further study, specifically in relation to environmental interactions and long term effects.

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4. CHEMICAL FAILURE MODES OF TYPE 304L STAINLESS STEEL

Type 304L-SS (stainless steel) is a current candidate material to be used as part of the HLW package. It would be used as the mold in which the waste glass is processed. Thus, it may be considered an integral part of the waste form which can contribute to some period of containment of radionuclides before it is breached and allows repository water to contact the glass.

The Type 304L stainless steel is not considered to be the primary barrier against corrosion (the overpack which surrounds the waste container provides this function), however, it will survive for some period of time under repository conditions. The chemical and mechanical failure modes of Type 304L stainless steel will determine the containment capability.

The primary modes of possible chemical failure for Type 304L-SS are uniform, pitting, crevice, and galvanic corrosion, stress corrosion cracking (SCC), and hydrogen embrittlement.

4.1 Uniform Corrosion

Braithwaite and Molecke¹ have discussed the variables which will affect the uniform corrosion rate. They include temperature, pressure, groundwater composition, pH, Eh, and radiation. The present available data regarding anticipated environmental conditions in salt and basalt host rock repositories have recently been evaluated.² The actual conditions which the waste package encounters will be determined by the final design (e.g., temperature will be a function of waste loading and the presence of backfill).

Several materials were exposed to deoxygenated brines and seawater at 250°C for 28 days.¹ The corrosion rates for Type 304L-SS in WIPP Brine A, Brine B, and seawater were reported to be 18, 10, and 6 $\mu\text{m}/\text{yr}$ respectively.

PNL³ exposed 22 different metals to MgCl_2 -NaCl brine at 250°C for up to 72 days. The brine solution composition is given in Table 4.1. The descaled weight change for Type 304L-SS was reported to be $-5\text{mg}/\text{dm}^2$ (~ 0.32 $\mu\text{m}/\text{yr}$).

The corrosion behavior of Type 304L-SS was also investigated in Hanford basaltic groundwater at 250°C. The groundwater composition is given in Table 4.2. The major difference between the first and second test was the oxygen content in the solution. The descaled weight change for the first three months was reported to be -0.9 mg/dm^2 (~ 0.046 $\mu\text{m}/\text{yr}$) and that for the second three months was -1.5 mg/dm^2 (~ 0.076 $\mu\text{m}/\text{yr}$).

Type 304L-SS possesses excellent resistance to uniform corrosion in both brine and basaltic water environments and appears unlikely to fail first by this mode.

Table 4.1

PNL Brine Solution Composition³

Ions	Makeup
Mg ⁺²	34.98 g/L
Na ⁺	41.34 g/L
K ⁺	29.95 g/L
Ca ⁺²	0.60 g/L
Li ⁺	20 mg/L
Rb ⁺	20 mg/L
Sr ⁺²	5.3 mg/L
Cs ⁺	0.8 mg/L
Cl ⁻	191.3 g/L
SO ₄ ⁻²	3.51 g/L
BO ₃ ⁻³	1.24 g/L
Br ⁻	0.39 g/L
I ⁻	10 mg/L
Fe ⁺²	2 mg/L

Table 4.2

Synthetic Hanford Groundwater Formulations³

Ion	August 1979 to May 1980		May 1980 to July 1980	
	Makeup, mg/L	Analyses,* mg/L	Makeup, mg/L	Analyses,* mg/L
Al ⁺³	0	10	0	6
Na ⁺	139	140	111	127
Mg ⁺²	0.5	0.05	0.5	0.05
Ca ⁺²	1.6	0.1	2.5	0.1
K ⁺	13	55	13	21
CO ₃ ⁻² (Total)	167	210	167	240
SiO ₂	36.	210	36	331
Cl ⁻	52	50	52	58
F ⁻	8	8	8	8
SO ₄ ⁻²	0.8	--	0.8	5
O ₂ , ppm	<1	--	<0.05	--
pH	9.5	8.5	9.0	7.7
Conductivity, μmho	475	55	630	600

*Sample was cooled before sampling. The water passed through a bed of crushed basalt at 250°C in the autoclave, which increased the Al and Si, and decreased pH, Ca, and Mg.

4.2 Pitting Corrosion

Pitting is a form of localized attack that usually occurs in stainless steels where passivity has been destroyed. Once the passivity has been lost in a local spot, the area will be anodic to the remaining passive surface. The subsequent development of these active anode areas into pits will depend upon the current flowing between the small anodic area and the large cathodic area around the pit.

A number of theories have been proposed to explain the initiation of pits using both kinetic and thermodynamic approaches. Shreir⁴ and Szklarska-Smialowska⁵ have reviewed and discussed these theories in their publications. A mechanism for the propagation of pits proposed by Fontana⁶ is widely accepted. This mechanism is based on the migration of chloride ions to the pit and hydrolysis of the metal chloride which results in a pH drop in the pit.

There are many environmental variables which can influence pitting behavior. Increasing the chloride concentration of a solution significantly increases the tendency for pitting. Of the other halogen ions, bromides will also cause pitting, but fluoride and iodide solutions do not promote pitting. Among metal ions cupric, ferric, and mercuric ions in chloride solutions are particularly aggressive.⁷ Among anions that reduce the tendency to pit in chloride solutions, as indicated by a displacement of the pitting potential in the noble direction, are SO_4^{-2} , OH^- , ClO_4^{-2} , and NO_3^- . Their inhibiting effects depend upon their concentrations and the concentrations of chloride ions in the solution.⁸

An increase in temperature generally results in an increased tendency for pitting. The decrease in pitting potential with increasing temperature is shown in Figure 4.1.⁹ It has been observed that pitting attack may increase abruptly once some critical temperature has been exceeded. Tests by Brennert¹⁰ in 3-normal sodium chloride solution indicated a critical temperature of about 130°F (54°C) for Type 304-SS. Similarly Uhlig¹¹ found that with Type 304-SS corrosion tended to increase sharply above 140°F (60°C) and to reach a maximum at about 195°F (91°C). At higher temperatures the lower solubility of oxygen tended to reduce the intensity of pitting attack.

The effect of pH on pitting potential is shown in Figure 4.2.⁹ There is relatively little effect of pH in the range 1.6 to approximately 10. However, in alkaline solutions the pitting potential is significantly displaced in the noble direction due to the inhibiting effect of higher concentrations of OH^- ions.^{7,8}

4.3 Crevice Corrosion

Crevice corrosion may occur if a metal surface is shielded in such a way that areas of limited access to corrosive solutions exist. This type of corrosion shares much in common with pitting and SCC.⁵ Fontana and Greene⁶

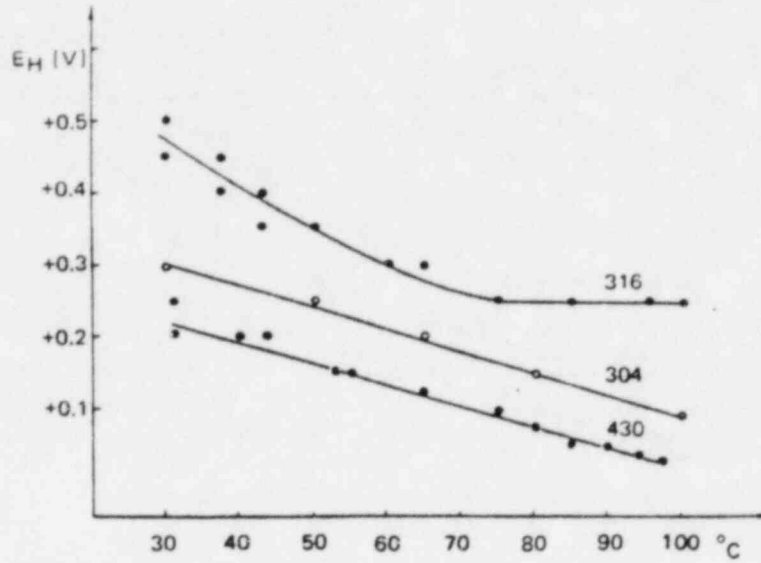


Figure 4.1 Effect of temperature on the pitting potential of various stainless steels in a 3% NaCl solution.⁹

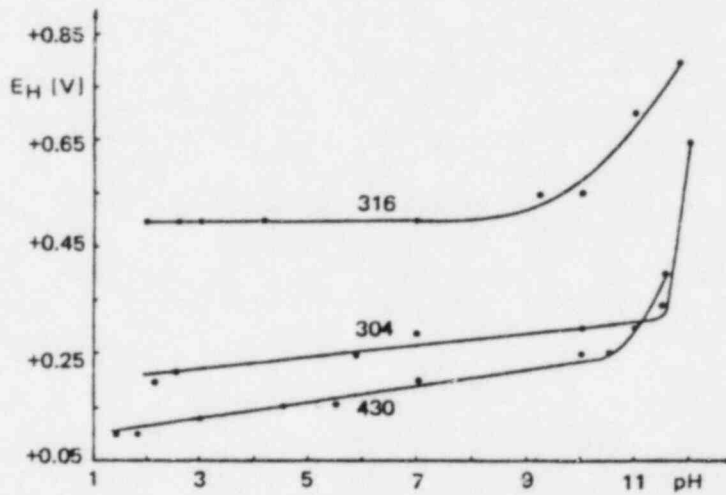


Figure 4.2 Effect of pH on the pitting potential of various stainless steels in a 3% NaCl solution.⁹

have proposed a unified mechanism applicable to stainless steels that incorporates many of the features of the earlier mechanisms (e.g. metal-ion, differential aeration and active passive cells).

Peterson and others¹² have reported intense crevice corrosion of Type 304-SS in seawater. Ellis and LaQue¹³ have shown that for stainless steel crevices in seawater, decreasing the crevice area or increasing the area of material outside the crevice (bold area) results in an increase in crevice attack. The importance of the cathode-to-anode area ratio on the probability of crevice corrosion initiation for Type 304-SS in seawater is shown in Figure 4.3.¹⁴

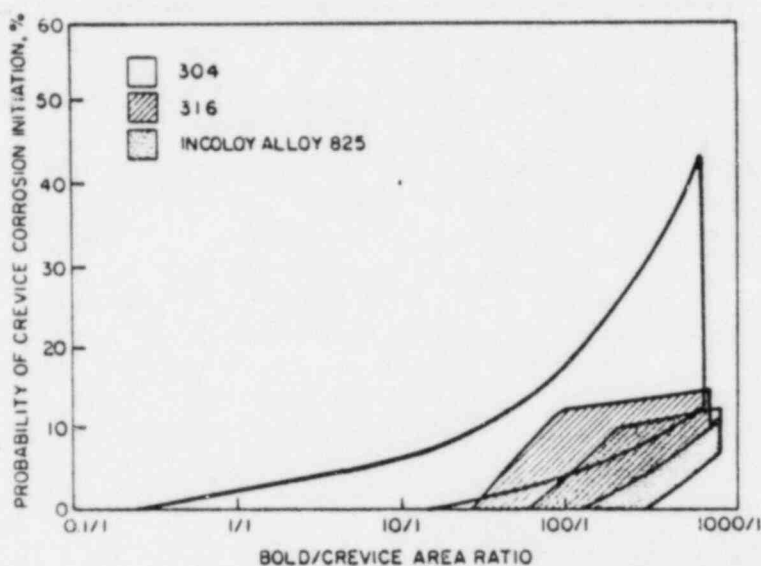


Figure 4.3 Probability of crevice corrosion initiation as a function of bold/crevice area ratio. Exposure conditions: 30 days in flowing ambient temperature seawater.¹⁴

The effect of increasing temperature on crevice corrosion is not easy to predict. Transport processes and reaction kinetics would be accelerated by increasing temperature but the solubility of oxygen would be reduced. The effect of seawater temperature on the probability of crevice corrosion initiation is given in Table 4.3. The maximum depth of crevice corrosion attack after a 30-day exposure to seawater at 15°C was reported to be 0.28 mm (~3.4 mm/yr).⁷

Braithwaite and Molecke exposed welded coupons with clamped crevices made from Type 304L-SS to deaerated WIPP Brine B at 70°C and 200°C.¹ Crevice corrosion problems were not reported in these deaerated solutions; however, numerous pits occurred around the welded areas at 70°C.

Table 4.3

Effect of Seawater Temperature on the Probability of Crevice Corrosion Initiation. Multiple Crevice Test, 30-Day Exposure⁷

Stainless Steel	Probability of Crevice Corrosion Initiation (Percent)			
	5°C	15°C	25°C	50°C
Type 304	2	13	70	90

4.4 Galvanic Corrosion

Galvanic corrosion occurs when two dissimilar metals in contact are immersed in a corrosive or conductive solution. The less corrosion resistant metal experiences increased attack while the corrosion rate of the more resistant metal is decreased, as compared with the behavior of these metals when they are not in contact.

The stainless steels are usually quite cathodic relative to other alloys but their potentials may vary over a wide range depending upon whether they are in an active or passive state. Type 304-SS in seawater has exhibited electrode potentials from -0.28 to +0.5 volts referred to the saturated calomel electrode.¹⁵ The Type 304L-SS may be expected to be cathodic to most of the common structural alloys such as ordinary steel or aluminum. This usually means a reduction in the normal corrosion rate of the Type 304L-SS and accelerated degradation of the anodic metal.

A present waste package design includes the use of a TiCode-12 overpack. TiCode-12 is highly corrosion resistant and is likely to possess a corrosion potential similar to Type 304L-SS. This implies that the galvanic corrosion effect in this couple is not expected to be severe. The Brookhaven National Laboratory report section on TiCode-12 galvanic corrosion behavior under waste repository conditions contains additional information regarding Type 304L-SS galvanic corrosion behavior as a waste package component.¹⁶

4.5 Stress Corrosion Cracking

With the austenitic steels, it is well known that failure by stress corrosion cracking can occur in chloride and caustic solutions.¹⁶ Figure 4.4 shows the effects of chloride level on the time for cracking of Type 304-SS in an aqueous NaCl solution.¹⁷ The specimens were stressed by bending strips into the form of a "U bend". The important point to note is that failure will occur for chloride concentrations between 10-1800 ppm if the tests are of sufficient duration. Short term laboratory tests, lasting for days or weeks, may be totally inadequate in the prediction of stress assisted failure.

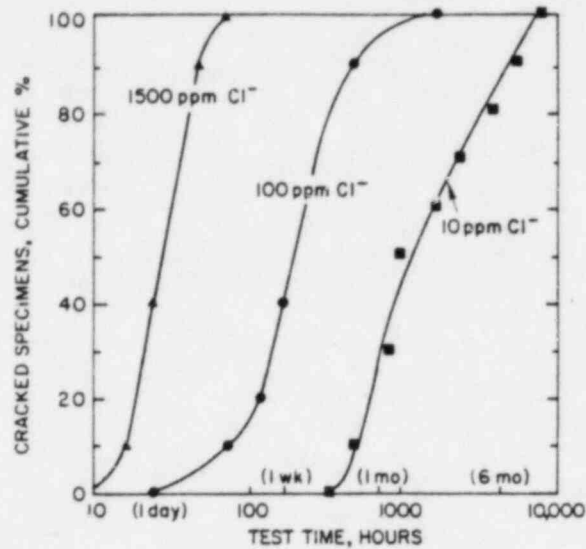


Figure 4.4 Effect of chloride concentration on the cracking susceptibility of Type 304 stainless steel exposed at 100°C under the concentrating conditions of the Wick Test.¹⁷

Oxygen also plays an important role in the SCC of austenitic stainless steels. In Figure 4.5 the conjoint action of oxygen and chloride levels is shown for Type 304-SS.¹⁸ High oxygen and chloride contents in the solution promote early failure. Work by Braithwaite and Molecke indicate that oxygen in water in the range of parts per billion could enhance chloride SCC.¹

Increasing exposure temperature is also known to accelerate the SCC of austenitic stainless steels in sodium chloride solutions. The traditional engineering viewpoint, based on practical experience,¹⁹ is that chloride cracking can occur at temperatures above 60°C provided that the material is exposed for very long times. The temperature dependence of chloride cracking is shown in Figure 4.6.²⁰

Type 304L-SS has been found to catastrophically fail by SCC in dilute chloride solutions at 49°C during a 2-year period of service in a feedwater deaerator system.²¹ The feedwater chloride content was about 160 ppm but the overall chloride level at the steel surface was probably much less. After careful analysis it was concluded that stress corrosion cracking induced by thermal gradients caused the failure.

Levy and others²² have shown that the expected radiation levels from an unshielded waste package could produce large quantities of colloidal sodium in salt. This raises the possibility of brine solutions containing large amounts of sodium hydroxide. It has been known for some time that for certain combinations of caustic concentration and temperature stainless steels can exhibit caustic cracking.^{23,24} A recent summary of available caustic cracking data for Type 304-SS indicates that there is an inherent danger of caustic cracking in strong caustic solutions when the temperature approaches 100°C.⁷

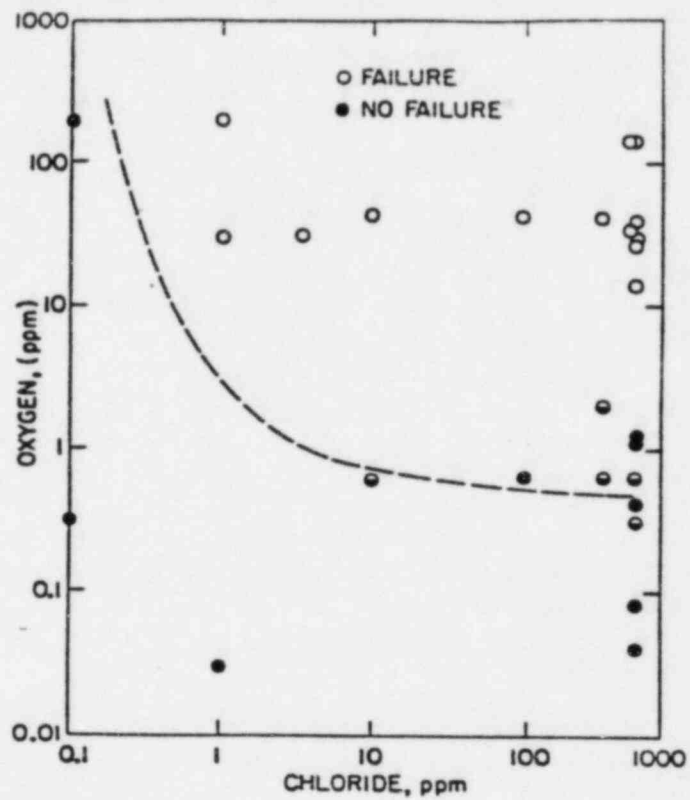


Figure 4.5 Relationship between chloride and oxygen content of alkaline-phosphate treated boiler water and susceptibility to stress corrosion of austenitic stainless steel exposed to the steam phase with intermittent wetting.¹⁸

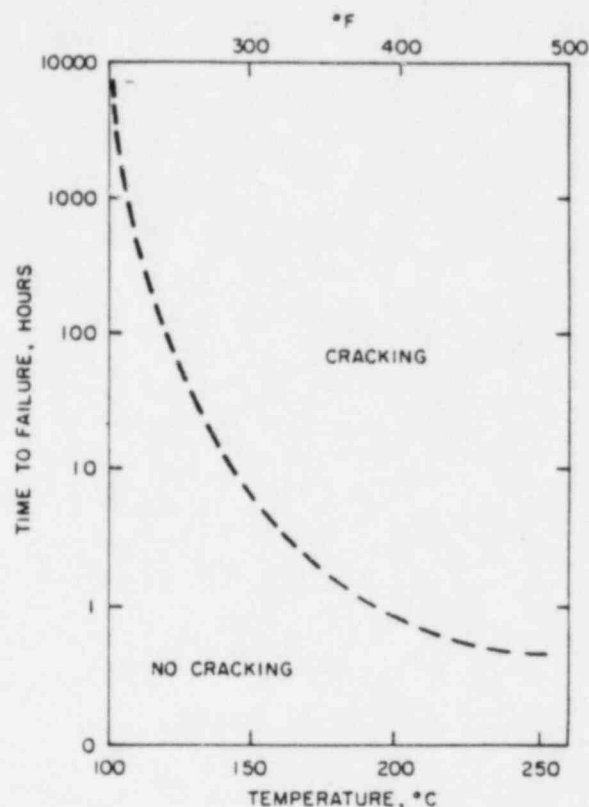


Figure 4.6 Effect of temperature on the chloride cracking resistance of Type 304 and 347 stainless steels in 0.1-33.0% sodium chloride solution containing oxygen.²⁰

More detailed descriptions of SCC of austenitic stainless steels in chloride and other environments are given in References 7, 25 and 26.

4.6 Hydrogen Embrittlement

The source of hydrogen in repositories is likely to be a natural consequence of aqueous corrosion, but it may also be generated by the radiolysis of water by gamma irradiation. The austenitic stainless steels are a frequent choice for immunity to hydrogen embrittlement, however, hydrogen embrittlement has been identified in Types 304 and Type 304L stainless steel.^{27,28}

Eliezer²⁹ has studied the hydrogen embrittlement of type Type 304L-SS by cathodic charging of thin tensile specimens. Hydrogen induced slow crack growth was observed at room temperature when the specimen was stressed while undergoing cathodic charging. Room temperature cathodic charging of unstressed specimens for 15 days resulted in intergranular attack during subsequent tensile testing in air.

The ductility loss in Type 304L-SS in the presence of hydrogen has been studied by Thompson.³⁰ The elongation of sheet specimens was measured without exposure, and after exposure for two months at 475°K (202°C) in air and also hydrogen at a pressure of 69 MPa. It was found that the Type 304L-SS experiences a sharp decrease in ductility of about 50 percent as shown in Figure 4.7. The proposed mechanism involves dislocation transport of hydrogen and accumulation of the hydrogen at interfaces between the matrix and non-metallic inclusion particles. Fracture then occurs by normal, though accelerated, ductile rupture processes.

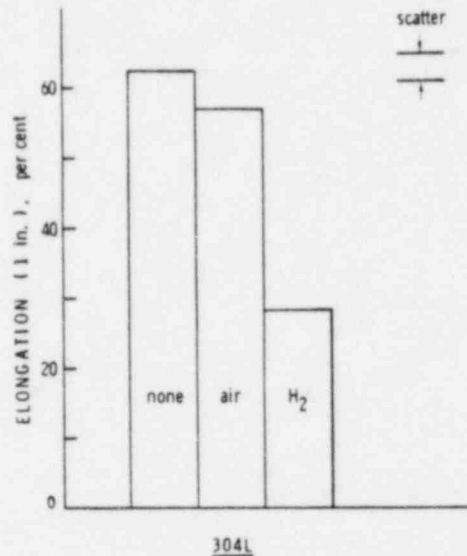


Figure 4.7 Ductility (elongation) of Type 304L-SS sheet specimens after the exposures shown: as-annealed; in air for two months at 202°C; or in hydrogen for two months at 202°C.

West and Brooks³¹ reported that tensile tests on Type 304L-SS gas-tungsten-arc welds showed large ductility losses (~50% loss in reduction in area) during high pressure hydrogen testing (69 MPa H₂). This was accompanied by a change in fracture mode from ductile dimple fracture when tested in air to fracture along the $\gamma - \delta$ boundaries when tested in hydrogen. A model based on hydrogen transport by dislocations was proposed to account for the observed behavior.

4.7 Additional Data Required to Characterize Type 304L Stainless Steel Chemical Failure Modes

The quantity of data available is, at present, insufficient to adequately characterize Type 304L-SS corrosion behavior under waste repository conditions. Since Type 304L-SS has not been considered as the primary corrosion barrier, extensive testing in brines and basaltic waters at high temperatures and radiation doses is lacking.

In order to estimate the containment period for a Type 304L-SS mold an understanding of the mechanisms operating in the various forms of corrosion is required. The development of models and predictive equations from long term testing is also a necessity.

The uniform corrosion rates of Type 304L-SS in brines and basaltic waters are reported to be small. The corrosion scale and products, however, have not been indentified in these tests. The effects of radiation exposure were also not studied. In an unshielded waste package this would lead to the radiolysis of the solutions and possible sodium hydroxide production.

Pitting studies under repository conditions are required. Testing under the various conditions of temperature, radiation, solutions, etc. should be performed. A characterization of the environment in and surrounding the pit would aid in the determination of the controlling mechanisms. Statistical analyses to characterize pitting behavior are required using long term test data.

Crevice corrosion rates under repository conditions are needed. The effects of geometry, temperature, oxygen, pH, radiation and solution ions should be established.

Galvanic corrosion effects of Type 304L-SS coupled with other candidate metallic waste components need to be studied. This includes the determination of the corrosion products, corrosion rates, and the cathode to anode ratio effect.

Long term testing of SSC specimens should be conducted. The effects of temperature and solution species must also be considered. Fracture mechanics specimens would be useful in obtaining critical stress intensities for crack propagation.

Further testing at various hydrogen levels to determine the effects on various mechanical properties should be performed. The rate of hydrogen uptake and mechanisms of embrittlement should also be studied.

4.8 Summary and Conclusions

The data available are inadequate to characterize the corrosion behavior of Type 304L stainless steel under repository conditions. Preliminary conclusions concerning the various possible failure modes are as follows:

- Failure by SCC is a serious problem. Cracking occurs in both chloride and caustic solutions. Extensive testing is required since this is the most likely mechanism by which early failure will occur.
- Pitting often occurs in chloride environments. This is likely to cause problems in a salt repository. Conditions in a basalt repository are more favorable.

- Crevice corrosion is also a potential problem. Again it is likely to be more severe in a salt repository than in a basalt repository.
- Hydrogen environments have been shown to result in a loss of ductility during tensile testing.
- Type 304L is highly resistant to uniform corrosion and unlikely to fail by this mechanism.
- Galvanic corrosion effects are expected to be small and unlikely to be a problem.

Predicting long term behavior will involve testing over long periods. This is lacking in all studies of Type 304L-SS to date. Studies of Type 304L-SS under the expected repository conditions should include testing in the various repository waters and at the temperatures and radiation doses expected. For an unshielded waste package in salt, the effects of sodium hydroxide should also be studied. Testing for the various corrosion modes should be performed with welded as well as with base metal specimens.

There remains a large amount of additional data required to characterize Type 304L-SS corrosion behavior. They include:

- Determination of long term uniform corrosion rates under repository conditions and identification of corrosion scales, products and mechanisms.
- A characterization of pitting phenomenon which includes statistical analyses of pitting frequency and depths.
- Crevice corrosion rates and effects of geometry and environment.
- Galvanic corrosion testing of Type 304L-SS coupled with other metallic waste components and data regarding corrosion products, accelerated rates and the cathode to anode ratio effect.
- Long term SCC testing under expected repository conditions to determine effects of environmental parameters, critical stress intensity values and times to failure.
- The effect of varying hydrogen levels on the various mechanical properties of Type 304L-SS.

4.9 References

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5. MECHANICAL FAILURE MODES OF TYPE 304L STAINLESS STEEL

The Type 304L stainless steel component of the waste form functions primarily as a mold to contain the waste glass during processing rather than as a structural element. The waste package container (and possibly an emplacement sleeve) would be designed to provide the basic mechanical strength and support for the waste package system. However, fracturing or rupturing of the Type 304L-SS could occur and permit groundwater to leach radionuclides from the waste glass.

5.1 Residual Stresses

The residual stresses in the Type 304L-SS result from the processing of the glass and any welding which is performed. The thermal expansion coefficient of the steel is about twice that of glass. After filling, cooling causes the steel to contract tightly around the solidified glass resulting in residual tensile stresses in the metal. Residual stresses have been measured in canisters filled by the in can melt process and have consistently been found to be nearly equal to the yield strength of the mold material.¹ The stainless steel is tough and ductile so that the residual stresses should not cause brittle fracture. Also, the number of stress cycles are few so that the effect of residual stresses on fatigue life are not of concern. Failure by stress rupture is also unlikely at the low temperatures involved. Stress corrosion cracking and hydrogen embrittlement are two major possible failure modes and have been addressed in the section on chemical failure modes of Type 304L-SS elsewhere in this report. Sensitization of the steel during processing or welding should also be avoided if possible since it can lead to intergranular corrosion and failure.

5.2 Radiation Induced Stresses

Cracking by radiation is not likely to occur for the doses expected. However, the heat generated by radiation can give rise to stress relaxation which would be beneficial.

Radiation can indirectly produce stresses through its effects on the density of the glass. Volume changes in borosilicate glasses have been reported to be as high as $\pm 1\%$ ² which can generate tensile stresses in the Type 304L-SS during the radionuclide containment period.

5.3 Lithostatic and Hydrostatic Pressures

The lithostatic and hydrostatic pressures at a repository depth can be approximately as high as 35 MPa.³ This is much lower than the typical tensile strength of Type 304L-SS (~ 520 MPa⁴). However, the actual external stress which the Type 304L-SS will be subjected to will depend upon the waste package design. The total external pressure will be distributed among the various waste package components. The container system and emplacement sleeve, if used, would provide the main support. The waste glass around which the Type 304L-SS is positioned should also provide some support against

crushing or buckling of the stainless steel. Some waste form designs, however, have an unfilled space at the top of the canister or an assembly gap which could create high stress concentrations if the external container mechanically failed.⁵ (See Figure 5.1.) This is not foreseen as a major problem since the use of a reinforced head or filler material or other design option could relieve the situation.

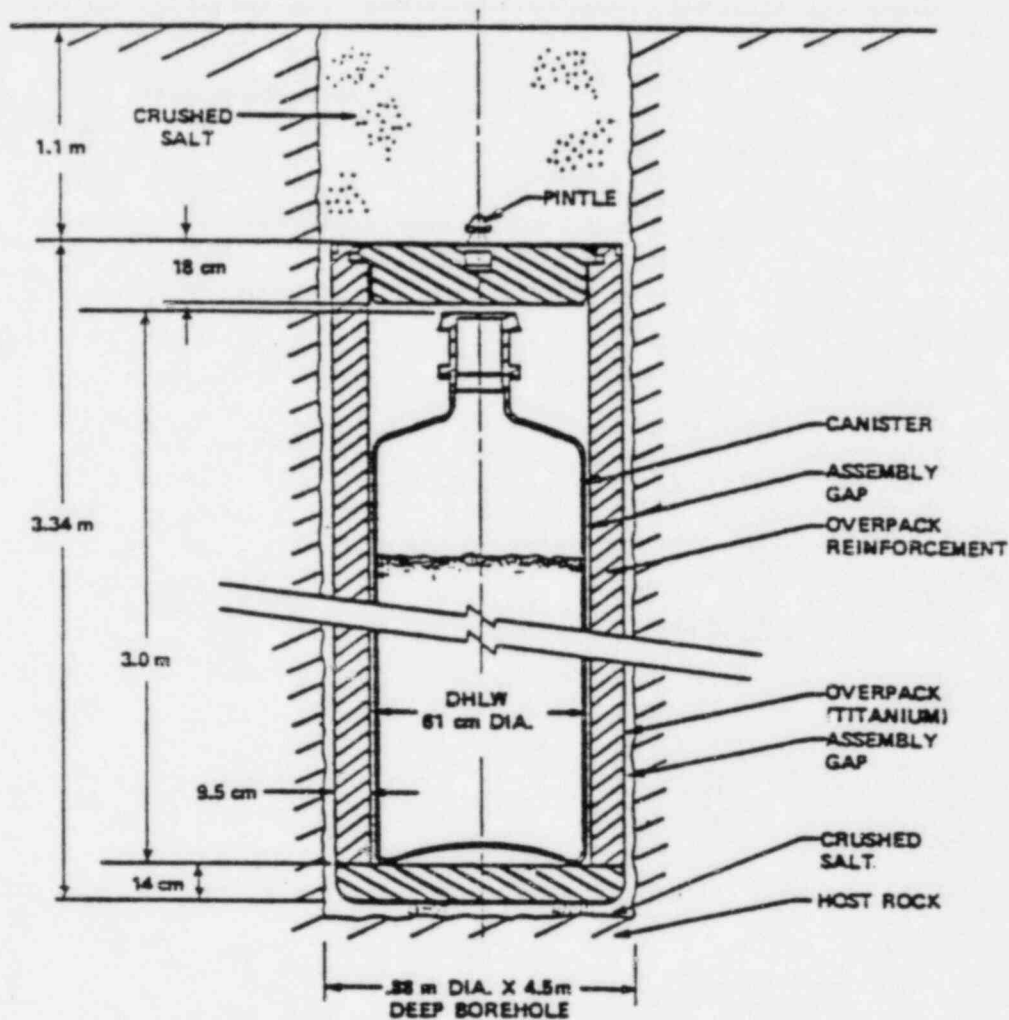


Figure 5.1 Reference DHLW Package for Borehole Emplacement in Salt⁵

There also exists the possibility of seismic activity or movement of host rock which can result in high shear stresses. Pusch⁶ had addressed this problem in granite host rock. It was concluded that copper containers could possibly fail in this manner and that high strength steels were superior.

5.4 Additional Data Requirements for Characterization of Type 304L-SS Mechanical Failure Modes

The states of stress which the Type 304L-SS will be subjected to will determine the modes of mechanical failure. There exist residual stresses from welding and glass solidification which should be studied and quantified. Radiation will also induce stresses both directly and indirectly. The levels and states of stresses Type 304L-SS experiences should be measured or calculated. It is very important to minimize all stresses since stress corrosion cracking is a recognized problem.

The external stress to which Type 304L-SS will be subjected, should be better quantified and understood. In this case, to insure mechanical integrity, the thickness of the Type 304L-SS can always be increased to counter the expected stresses. The geologic stresses caused by host rock movement in salt and basaltic rock should be studied to determine if rupture of the Type 304L-SS can occur as a result of seismic activity.

5.5 Summary and Conclusions

Residual, radiation induced, and external stresses can all contribute to the mechanical failure of Type 304L-SS. Creep, fatigue, and brittle fracture are unlikely modes of failure under repository conditions. Stress corrosion cracking and rupture from external stresses are potential problems and must be avoided. Reduction in stress levels could be achieved through various design and fabrication processes (e.g., reinforcement of the stainless steel, elimination of gaps between waste package components, use of heat treatments to reduce residual stresses, use of thicker sections to support the load, etc.).

The additional data required to characterize Type 304L-SS mechanical failure modes are:

- Determination of the magnitudes and states of stress resulting from radiation, welding, and manufacturing. Stress corrosion cracking is a serious problem and must be investigated (see Section 4).
- The external pressures exerted by the host rock should be measured. The probabilities and magnitudes of shear stresses caused by salt and basalt host rock movements should be assessed.
- The stresses the Type 304L-SS will encounter are to a large extent design dependent. The optimum Type 304L-SS thickness, use of reinforced head, thickness of container walls, etc. should all be determined.

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