

**IDENTIFICATION OF AREAS FOR DEVELOPING
UNDERSTANDING OF LONG-TERM PERFORMANCE OF
BOROSILICATE GLASS WASTE FORM**

BASED ON

**"HIGH-LEVEL WASTE BOROSILICATE GLASS:
A COMPENDIUM OF CORROSION CHARACTERISTICS"
DOE-EM-0177**

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ABSTRACT

This report identifies the areas requiring additional effort for developing a better understanding of the mechanisms involved in the corrosion of glass waste forms, primarily the borosilicate glass, when exposed to an aqueous environment. The ultimate need for such information is to be able to support evaluation of the acceptability of the glass waste form for disposal in a geologic repository. The principal source of information for the areas identified as requiring further effort in this report was Volume I of the report titled, "High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics," DOE-EM-0177, March 1994. Volume II of the report, which provides more detailed information of the subjects covered in Volume I and the experimental data, was also consulted as appropriate. Although considerable information is available on the behavior of borosilicate glass when exposed to an aqueous environment, there are a number of gaps in the fundamental understanding of the long-term performance of the glass waste forms. The gaps are in the areas of mechanisms of corrosion and completeness of the data bases for developing or validating long-term performance models. Specific examples include:

- Glass corrosion kinetics in Stage 3 (beyond the laboratory testing time frame)
- Effects of the composition of glass on its long-term performance
- Data on the influence of engineered barrier system (EBS) and repository construction materials on the acceleration of glass corrosion
- Devitrification kinetics at temperatures below glass transition temperature
- Thermodynamic properties of the stable and metastable phases formed in altered surface layers
- Incorporation into the glass performance models of release of radionuclides via colloids
- Linkage between models for glass corrosion rate and repository performance

It is concluded that, at present, a model that can predict the long-term performance of borosilicate glass in an aqueous environment and which could be used for licensing the vitrified waste form for disposal in an unsaturated repository is not available. However, it is also recognized that there are a number of ongoing investigations and analytical efforts for developing the required knowledge. Such efforts are expected to yield information and data that will form the basis for the judgement on the acceptability of a borosilicate glass waste form for disposal in a geologic repository.

CONTENTS

Section	Page
ACKNOWLEDGMENTS	vii
1 INTRODUCTION	1-1
2 GENERAL COMMENTS	2-1
2.1 COMMENTS	2-1
3 SPECIFIC COMMENTS AND QUESTIONS	3-1
3.1 COMMENTS	3-1
3.2 QUESTIONS	3-16
4 SUMMARY	4-1
5 REFERENCES	5-1

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1 INTRODUCTION

Current plans for the management of high-level nuclear waste (HLW) stored in the United States involve converting the waste into a canistered borosilicate glass form "acceptable for disposal" in a deep mined geologic repository (U.S. Department of Energy, 1991). After a period of interim storage, the intent is that this canistered borosilicate waste glass will be transported to a geological repository location and packaged for final disposal. Over the past few decades, a large body of scientific information on borosilicate waste glass has been generated worldwide. A recent U.S. Department of Energy (DOE) report (referred to hereafter as the "Compendium") documents such information—which includes qualitative information, data, and analyses related to vitrified waste forms, primarily borosilicate glass, for incorporation of HLW generated primarily from defense activities in the United States (U.S. Department of Energy, 1994). (There is a very small quantity of HLW that was generated from reprocessing of the spent fuel from commercial reactors. This waste, currently stored at the West Valley site in New York, is also planned to be incorporated in borosilicate glass.)

Using the Compendium as the basis, this report identifies areas requiring additional effort for developing a better understanding of the long-term performance of borosilicate glass. The principal source of information for the areas identified as requiring further effort in this report was Volume I of the Compendium. Volume II of the Compendium, which provides more detailed information of the subjects covered in Volume I and the experimental data, was also consulted as appropriate. A number of comments or questions have been presented in this report. (The figure and tables referred to in the Comments and Questions are from Volume I of the Compendium.) These comments and questions cover a broad range of areas including waste composition and glass formulations, processing, storage prior to repository disposal, performance in a geologic environment under a number of credible scenarios including weathering and corrosion, and modeling of performance from the viewpoint of long-term isolation in a geologically unsaturated environment. The comments and questions, which are followed by recommendations, are directed generally to the United States program rather than to the authors of the Compendium, as it is recognized that the scope of the Compendium does not cover all areas of interest for licensing of the glass waste for repository disposal.

References:

- U.S. Department of Energy. 1991. *Five Year Plan 1993-1997: Environmental Restoration and Waste Management*. DOE-S-0089. Washington, DC: U.S. Department of Energy.
- U.S. Department of Energy. 1994. *High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics*. DOE-EM-0177. Washington, DC: U.S. Department of Energy.

2 GENERAL COMMENTS

2.1 COMMENTS

COMMENT 1

Glass corrosion kinetics in Stage 3 are not well understood.

Basis:

The Compendium describes the glass corrosion in three stages. Stage 1 corresponds to an initial transient period when ion exchange is dominant. Stage 2, which spans the duration of most laboratory tests, is characterized by hydrolysis and dissolution of the glass network. Stage 3 corresponds to times beyond the experimentally accessible times for laboratory testing. Although glass corrosion during Stage 3 is believed to involve the same reactions as in Stages 1 and 2, the record of evidence for the dominant reactions is comparatively sparse. The relative importance of ion exchange, network hydrolysis, and dissolution contributions to long-term corrosion has not been established. The performance of glass waste form under repository conditions needs to be based on the understanding of the mechanism of degradation relevant to the time frame of regulatory interest. Of the three stages, glass corrosion in Stage 3 is of most interest from a repository licensing point of view. Performance in this stage is likely to be influenced by factors both internal and external to the glass [e.g., composition of glass, corrosion products of the engineered barrier system (EBS), backfill and repository closure materials, and geochemistry and geology of the site]. Current lack of understanding of the kinetics of glass corrosion in Stage 3 raises doubts about the ability to predict waste glass corrosion kinetics beyond the laboratory test time frame.

Recommendation:

Develop a better understanding of the mechanism that governs the glass corrosion in Stage 3 (long-term performance).

COMMENT 2

Current models are not successful in predicting glass corrosion rate as a function of glass composition.

Basis:

The effects of glass composition on the corrosion rate are complex. For example, Al increases the durability as measured by short-term tests while, under some conditions, it may reduce durability as measured by long-term tests. Although there are a lot of experimental data and modeling approaches for correlating short-term durabilities, the experimental evidence for the effects of glass composition on the longer-term corrosion rates is limited.

Recommendation:

Develop a better understanding of the influence of glass composition on its long-term performance. Such an understanding has the potential for providing added flexibility in designing (within processing constraints) glass formulations to optimize performance allocation for the waste form. It will also provide the basis of identifying a bounding glass composition, for testing and modeling, which could cover a number of glass compositions that may need to be fabricated because of necessity (e.g., existing inventories that cannot be mixed easily).

COMMENT 3

Current geochemical models predict several thermodynamically stable phases that are not observed under experimental conditions.

Basis:

Silicate glasses are metastable and, therefore, do not reach thermodynamic equilibrium with aqueous environments for long periods of time (hundreds to thousands of years or more).

Recommendation:

Performance assessment models should account for both thermodynamically metastable and stable phases that may form during glass corrosion under the repository environment and within the repository time frame.

COMMENT 4

The bulk of the data and conclusions about the performance of glass waste form are based on static leaching or drip tests. Data for flow-through conditions also need to be factored into the evaluations of glass corrosion.

Basis:

Three scenarios are likely during the long period of repository isolation of glass waste form. These are: (i) high-temperature humid environment, (ii) stagnant aqueous environment, and (iii) low-temperature aqueous flow-through environment. Extensive testing has been conducted for scenarios (i) and (ii), namely, high surface to volume (S/V) drip (weathering) tests, and MCC-1 and product consistency tests (PCTs) (aqueous corrosion). Both conditions (i) and (ii) result in formation of altered surface layers which are influenced considerably by the back-reactions due to saturation of the leachate with silica and possibly other compounds formed from elements released from the glass. The scenario represented by (iii) is different from scenarios (i) and (ii), namely, the leachate may never be saturated with silica and other elements due to flow-through condition.

Recommendation:

Identify flow-through test parameters that represent flow conditions in the repository, and determine the mechanism and reaction kinetics of glass corrosion under leachate flow-through conditions. Compare both short- and long-term corrosion kinetics for identical glass under both static and flow-through leachate tests. The performance models should incorporate both these glass degradation mechanisms for predicting long-term performance.

COMMENT 5

The Compendium does not provide adequate treatment of EBS and construction materials on the performance of glass waste form. Also, the influence of releases from spent fuel on glass corrosion is not discussed.

Basis:

Many of the human-introduced materials could have significant effect on the geochemistry of the repository. For example, EBS materials such as iron, aluminum, and bentonite clay could increase the rate of corrosion by causing removal of silicic acid from the leachate (e.g., by promoting the precipitation of silicate phases in the glass alteration layers or in the groundwater). In addition, repository construction materials such as cements and grouts could increase the pH of fluids with which they react to values as high as 11.5 (Meike, 1992). Oxidation of metals present in the repository can lower the oxidation state of the groundwater by reacting with dissolved oxygen and water. The degradation of the human-introduced materials is likely to generate colloids, which may increase the susceptibility of radionuclide transport to the far-field of the repository (Manaktala et al., 1995). The degradation of spent fuel may also influence the corrosion kinetics of glass.

Recommendation:

Influence of the EBS, repository construction materials, and the spent fuel on the corrosion kinetics of glass waste and on the release of radionuclides in colloidal form should be evaluated in detail and incorporated in repository performance assessment models.

References:

- Manaktala, H., D. Turner, T. Ahn, V. Colten-Bradley, and E. Bonano. 1995. *Potential Implications of Colloids on the Long-Term Performance of a High-Level Radioactive Waste Repository*. Draft Report. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.
- Meike, A. 1992. Man-made materials (Chapter 6). *Near Field Environment, Volume II: Scientific Overview of Near-Field Environment and Phenomena*. D.G. Wilder, ed. UCRL-LR-107476. Livermore, CA: Lawrence Livermore National Laboratory.
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COMMENT 6

The Compendium provides discussion of the capabilities and limitations of a number of performance assessment models for glass waste forms. However, it is unclear which model(s) would be preferred for predicting long-term performance of glass in the anticipated Yucca Mountain repository environment.

Basis:

Future/advanced development of performance assessment model(s) will depend on the assessment of the capabilities of the current models and identification of preferred model(s) for further development.

Recommendation:

Identify the model(s) suitable for further development into advanced model(s)—which could potentially be used for the licensing of the repository.

3 SPECIFIC COMMENTS AND QUESTIONS

3.1 COMMENTS

Section 1.2.2 Glass Corrosion Kinetics

COMMENT 1

Corrosion rates in Stage 3 are needed for modeling the long-term performance of glass waste form and for demonstrating compliance with the gradual release requirements of the regulations.

Basis:

Some compositions of glass waste forms may exhibit an increase in the corrosion rate near the end of Stage 2, at very high values of the reaction progress parameters, as shown schematically by the dashed lines in Figure 1-2. Although such effects have been explained qualitatively on the basis of the nucleation and precipitation of secondary phases that establish a lower saturation concentration of silicic acid (or other solution species) and thereby increase the affinity for glass dissolution, currently available experimental data for developing performance assessment models for West Valley and Savannah River glasses are inadequate.

Recommendation:

Better understanding of the effect of glass composition on Stage 3 corrosion rates should be developed. Data for Stage 3 corrosion rates for West Valley and Savannah River glass compositions need to be generated. Also, a bounding glass composition for generation of such experimental data should be established.

Section 1.2.4	Significance of Glass Corrosion and Radionuclide Release Data
Section 2.1.2.2.2	Cracking/Surface Area
Section 2.3.5	Repository Relevance

COMMENT 2

The estimate for the fraction (F) of the canistered waste that would corrode per year under saturation conditions shown in the Compendium, namely,

$$F = [2.5 \times 10^{-3} \text{ g/m}^2/\text{d}] [96 \text{ m}^2] [365 \text{ d/yr}] / [1.7 \times 10^6 \text{ g}] = 5.2 \times 10^{-5} \text{ yr}^{-1} \quad (3-1)$$

raises a concern regarding the contribution of the glass waste form towards meeting the gradual release requirements.

Basis:

The calculations show the fractional release to be $5.2 \times 10^{-5} \text{ yr}^{-1}$, but the maximum allowable release for most radionuclides is $1 \times 10^{-5} \text{ yr}^{-1}$. Therefore, glass, by itself, cannot be considered a sufficient barrier for meeting the release rate requirements. Furthermore, the estimated release is reported as not necessarily conservative but only a benchmark.

Recommendation:

Provide a fractional release estimate for a conservative case.

Section 1.2.4 Significance of Glass Corrosion and Radionuclide Release Rate Data

COMMENT 3

Based on the retention factors (RFs) for Np, Pu, and Am release from R7T7 glass (Vernaz and Dussosoy, 1992), it is reported that only a small fraction of the sparingly soluble radionuclides associated with the corroded glass are released (e.g., ~10% for Np, ~3% for Pu, and ~0.3% for Am). These numbers lead to fractional release rates for Np, Pu, and Am of $5.2 \times 10^{-6} \text{ yr}^{-1}$, $1.6 \times 10^{-6} \text{ yr}^{-1}$, and $1.6 \times 10^{-7} \text{ yr}^{-1}$, respectively. There is a concern that the values of RFs used in the calculations may not be appropriate for the West Valley and Savannah River glass compositions.

Basis:

Since RFs may be necessary for demonstrating compliance with the requirements of gradual release, the calculations should be based on values applicable to the West Valley and Savannah River glasses.

Recommendation:

Provide justification for the use of R7T7 glass data for the United States program. Also, confirm the validity of the 90 °C static deionized (DI) water leaching test for determining the RFs. Provide RF values for the Savannah River and West Valley glass compositions, and compare them with the values for French glass R7T7.

Reference:

Vernaz, E.Y., and J.L. Dussosoy. 1992. Current knowledge of nuclear waste glass dissolution mechanisms: The case of R7T7 glass. *Applied Geochemistry, Supplemental Issue 1*: 13-22.

Section 1.2.4 Significance of Glass Corrosion and Radionuclide Release Rate Data

COMMENT 4

The use of a factor of 20 multiplier to account for the increase in surface area of the glass as a result of cracking during cooling in estimating fractional release of radionuclides from a glass log does not appear to be justified.

Basis:

A wide variability in the increase of the surface area of glass due to cooling cracks (18 to 46 times) has been reported (Martin, 1985; Peters and Slate, 1981; Ross and Mendel, 1979; Slate et al., 1978). The upper bound of 46 times far exceeds the multiplier of 20 used for the calculations. Also, no consideration is given to the possibility of generating additional cracks and fractures during the anticipated two or more decades of storage and handling prior to transport of the glass waste form to a repository. There is also the possibility of generating additional cracks due to seismic events during the 10,000+ yr isolation at the repository.

Recommendation:

A more conservative value for the surface area increase due to cooling cracks should be used in fractional release calculations. A multiplier of 100+ is suggested for the bounding calculations. The use of suggested glass surface area increases the fractional rate shown in the Compendium of $5.2 \times 10^{-5} \text{ yr}^{-1}$ to $> 2.6 \times 10^{-4} \text{ yr}^{-1}$.

References:

- Martin, D.M. 1985. *Fracture in Glass/High Level Waste Canisters*. NUREG/CR-4198. Washington, DC: Nuclear Regulatory Commission.
- Peters, R.D., and S.C. Slate. 1981. *Fracturing of Simulated High-Level Waste Glass in Canisters*. PNL-3948. Richland, WA: Pacific Northwest Laboratories.
- Ross, W.A., and J.E. Mendel. 1979. *Annual Report on the Development and Characterization of Solidified Forms for High-Level Wastes—1978*. PNL-3060. Richland, WA: Pacific Northwest Laboratory.
- Slate, S.C., L.R. Bunnell, W.A. Ross, F.A. Simonen, and J.H. Westsik, Jr. 1978. *Stresses and Cracking in High-Level Waste Glass*. PNL-SA-7369. Richland, WA: Pacific Northwest Laboratory.
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Section 2.1.2.2.2 Cracking/Surface Area

COMMENT 5

In a study of fracturing of half-scale canistered waste forms under three cooling conditions (air cooling, insulated cooling, and water quenching), surface area increases by factors of 46, 21, and 24, respectively, have been reported (Martin, 1985). There is a concern related to the choice of the air cooling process for glass log fabrication as it corresponds to the largest increase in the surface area.

Basis:

The glass transition temperature of United States borosilicate waste glasses is reported to be 430 to 450 °C (Marra et al., 1992) (Figure 2-3). Therefore, to reduce cracking, water quenching is necessary only below about 450 °C. Cooling faster, by water quenching, in the 1150 to 450 °C range could provide an additional benefit of reducing the extent of devitrification of the glass.

Recommendation:

Optimize the glass cooling rate from the pour temperature to the ambient to reduce cracking and devitrification of glass.

References:

- Martin, D.M. 1985. *Fracture in Glass/High Level Waste Canisters*. NUREG/CR-4198. Washington, DC: Nuclear Regulatory Commission.
- Marra, S.L., R.E. Edwards, and C.M. Jantzen. 1992. Thermal history and crystallization characteristics of the DWPF glass waste form. *Proceedings of the Third International High Level Radioactive Waste Management Conference*. La Grange Park, IL: American Nuclear Society: 1: 917-924.
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Section 2.2.1.1 Temperature During Storage and Transportation

COMMENT 6

It has been reported that heat treatment of simulated HLW glasses for up to 100 hr at temperatures below the glass transition temperature resulted in no change in phase structure (Malow, 1989; Palmiter et al., 1991). On this basis, it is argued that by maintaining the temperature below 400 °C to satisfy the waste acceptance product specifications (WAPS) (U.S. Department of Energy, 1993), the phase structure of the glass should remain unchanged during transport within the vitrification facilities, in temporary storage, and during transport to the repository. There is a concern that the conclusions drawn from the annealing data may not be valid for the repository time frame.

Basis:

Since transformation leading to glass devitrification is a diffusion controlled process, it is likely that the transformation process will continue even at temperatures below the suggested cutoff temperature of

400 °C, albeit at a lower rate. Diffusivity at temperatures below the glass transition temperature is low, but not zero. Investigations to date have been limited only to 100 hr at temperatures below the glass transition temperature.

Recommendation:

Study and quantify the low-temperature devitrification (LTD) process for waste glasses through tests with much longer exposures at temperatures below the glass transition temperature (430 to 450 °C), but at high enough temperatures to be representative of the early period of the repository isolation of the wastes.

References:

- Malow, G. 1989. Thermal and radiation effects in the range of the glass transition temperature T_g . *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 127: 153-162.
- Palmiter, T.V., I. Joseph, L.D. Pye. 1991. Effects of heat treatment on the microstructure of a fully simulated nuclear waste glass. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 212: 153-158.
- U.S. Department of Energy. 1993. *Waste Acceptance Product Specifications (WAPS) for Vitrified High-Level Waste Forms*. EM-WAPS. Germantown, MD: U.S. Department of Energy.
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Section 3.1.1 Aqueous Corrosion

COMMENT 7

There is a concern that the use of bulk solution properties to explain corrosion of glass may not be valid as the properties of the leachate in the vicinity of the surface of the dissolving glass/gel could be quite different from bulk solution properties.

Basis:

It is likely that the fluid trapped inside the alteration rind of secondary phases has a chemistry that is controlled by the local environment (e.g., ion exchange with clays) and may not be well represented by bulk solution properties such as pH (Bunker, 1983). The mechanism for long-term glass dissolution may be explained more readily if a better understanding of the micro-environment at the glass-water reaction surfaces were available.

Recommendation:

Provide experimental data and discussion on the influence of the micro-environment in the vicinity of the dissolving glass/gel layer on the corrosion kinetics of the glass. Provide data on the pH and solution chemistry of the fluid trapped inside the alteration rind of secondary phases as a function of reaction progress.

Reference:

Bunker, B.C. 1987. Waste glass leaching: Chemistry and kinetics. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 84: 493-507.

Section 3.1.2 Waste Glass Weathering

COMMENT 8

Inherent instability (spallation) of the alteration surface layer on glass is of concern. The phenomenon of spallation could make it difficult to demonstrate compliance with the gradual radionuclide release requirement.

Basis:

In a series of tests developed specifically to study the reaction of HLW glass when exposed to dynamic weathering, the glass was contacted with controlled amounts of dripping water at 90 °C (Bates and Gerding, 1985; 1986; 1990). These tests, of 6+ yr duration, have monitored the reacted glass surface, the release of glass components, and the actinide elements. Spallation of the reacted surface layers has been observed in these tests as the glass underwent periodic wet-dry exposures. Also, the surface layers are reported to contain numerous channels for transport of aqueous species; indicating that they do not provide a coherent transport barrier over the glass surface (Abrajano et al., 1990; Lutze, 1988). Spallation has also been observed in other test configurations (Woodland et al., 1991).

Recommendation:

Develop a mechanistic understanding of and generate data on the cyclic nature of surface alteration layers, namely, formation and spallation. Include the instability characteristics of the altered surface layers on glass in modeling release of radionuclides from the glass.

References:

- Bates, J.K., and T.J. Gerding. 1985. *NNWSI Phase II Materials Interaction Test Procedure and Preliminary Results*. ANL-84-81. Argonne, IL: Argonne National Laboratory.
- Bates, J.K., and T.J. Gerding. 1986. *One-Year Results of the NNWSI Unsaturated Test Procedure: SRL 165 Glass Applications*. ANL-85-41. Argonne, IL: Argonne National Laboratory.
- Bates, J.K., and T.J. Gerding. 1990. *Application of the NNWSI Unsaturated Test Method to Actinide-Doped SRL 165 Type Glass*. ANL-89-24. Argonne, IL: Argonne National Laboratory.
- Abrajano, T.A., J.K. Bates, A.B. Woodland, J.P. Bradley, and W.L. Bourcier. 1990. Secondary phase formation during nuclear waste-glass dissolution. *Clays and Clay Mineralogy* 38: 537-548.
- Lutze, W. 1988. Silicate glasses. *Radioactive Waste Forms for the Future*. W. Lutze and R.C. Ewing, eds. Amsterdam: North Holland Publishers.

Woodland, A.B., J.K. Bates, and T.J. Gerding. 1991. *Parametric Effects on Glass Reaction in the Unsaturated Test Method*. ANL-91/36. Argonne, IL: Argonne National Laboratory.

Section 3.1.2 Waste Glass Weathering

COMMENT 9

There is a concern that alteration layers formed on the surface of corroding glass may transform from amorphous to crystalline phases with the reaction progress leading to acceleration of glass corrosion.

Basis:

Secondary crystalline phases form on the glass surface as a result of restructuring of the amorphous layers formed initially. The formation of such crystalline secondary phases has been related to observed increases in the reaction rate. These increases have been explained by the onset of the formation of specific crystalline phases which results in a decrease in the solution concentration of elements that control the reaction affinity of the glass (Ebert et al., 1991). The introduction of EBS components, spent fuel, and repository construction materials could further complicate and perhaps accelerate the transformation process.

Recommendation:

Develop a detailed understanding of the mechanism of transformation of alteration layers from amorphous to crystalline, including the influence of EBS components, spent fuel, and repository construction materials, and the consequences of such transformation on the long-term corrosion kinetics of the glass.

Reference:

Ebert, W.L., J.K. Bates, and W.L. Bourcier. 1991. The hydration of borosilicate waste glass in liquid water and steam at 200 °C. *Waste Management* 11: 205-221.

Section 3.2.1 Corrosion Rate

COMMENT 10

There is a concern that considerable uncertainty exists related to the detrimental effects of elements such as Al and Fe on the corrosion of glass.

Basis:

Laboratory tests have indicated that while Al may increase durability during Stage 1, it may increase the corrosion rate during Stage 2 (Smets and Lommen, 1982; van Iseghem and Grambow, 1988). Some closed-system leach tests of powdered glasses (Feng et al., 1989; Kinoshita et al., 1991) have shown that relatively small compositional differences can give rise to large differences in glass durability. A large increase in durability was observed when only 2 to 3 weight percent of silica was added to a base West

Valley WV205 glass composition. In addition, increase in glass corrosion have been reported in the presence of Fe in the leachate (McVay and Buckwalter, 1983).

Recommendation:

Provide the mechanism and data related to the effects of glass composition and multi-purpose canister (MPC) materials on the corrosion kinetics of glass, with particular attention on Al and Fe released from the MPC.

References:

- Smets, B.M.J., and T.P.A. Lommen. 1982. The leaching of sodium aluminosilicate glasses studied by secondary ion mass spectrometry. *Physical Chemistry of Glasses*. 23: 83-87.
- van Iseghem, P., and B. Grambow. 1988. The long-term corrosion and modelling of two simulated Belgian reference high-level waste glasses. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 112: 631-639.
- Feng, X., I.L. Pegg, A. Barkatt, P.B. Macedo, S.J. Cucinell, and S. Lai. 1989. Correlation between composition effects on glass durability and the structural role of the constituent oxides. *Nuclear Technology* 85: 334-345.
- Kinoshita, M., M. Harada, Y. Sato, and Y. Hariguchi. 1991. Percolation phenomena for dissolution of sodium borosilicate glasses in aqueous solutions. *Journal of the American Ceramic Society* 74: 83-87.
- McVay, G.L., and C.Q. Buckwalter. 1983. Effect of iron on waste-glass leaching. *Journal of the American Ceramic Society* 66(3): 170-174.
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Section 3.2.1 Corrosion Rate

COMMENT 11

Hydration theory does not appear to provide sufficient (or appropriate) means for predicting the durability of Defense Waste Processing Facility (DWPF) borosilicate glasses.

Basis:

The hydration theory, which correlates glass durability with an estimated free energy of hydration of glass, has been described in the literature as a method for determining glass durability (Paul, 1977; 1990). The DWPF glass durability estimates have been based on this theory (Jantzen, 1991; Plodinec et al., 1984). However, hydration theory alone is unable to predict the relative durabilities of borosilicate glasses (Bunker, 1987) and other simple glasses (Perera et al., 1991). The Compendium points out that empirical regression models of glass composition versus durability can provide better correlations with experimental data than hydration theory (Abrajano et al., 1988a).

Recommendation:

Hydration theory should be combined with the glass corrosion kinetics to predict the durability of borosilicate glasses containing the radioactive wastes.

References:

- Paul, A. 1977. Chemical durability of glasses: A thermodynamic approach. *Journal of Materials Science* 12: 2,246-2,268.
- Paul, A. 1990. *Chemistry of Glasses*. 2nd edition. New York: Chapman & Hall Limited.
- Jantzen, C.M. 1991. *Relationship of Glass Composition to Glass Viscosity, Resistivity, Liquidus Temperature, and Durability: First Principles Process-Product Models for Vitrification of Nuclear Waste*. WSRC-MS-91-011. Aiken, SC: Westinghouse Savannah River Company.
- Plodinec, M.J., C.M. Jantzen, and G.C. Wicks. 1984. Stability of radioactive waste glasses assessed from hydration thermodynamics. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 26: 755-762.
- Bunker, B.C. 1987. Waste glass leaching: Chemistry and kinetics. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 84: 493-507.
- Perera, G., R.H. Doremus, and W. Lanford. 1991. Dissolution rates of silicate glasses in water at pH 7. *Journal of the American Ceramic Society* 74: 1,269-1,274.
- Abrajano, T.A., J.K. Bates, and J.K. Bohlke. 1988a. Linear free energy relationships in glass corrosion. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 125: 383-392.

Section 3.2.1 Corrosion Rate

COMMENT 12

Correlation of short-term performance with long-term performance of glass, even within the laboratory time scale, is not considered reliable. This raises concerns about the ability to extrapolate results to the period of regulatory concern (i.e., 10,000 yr).

Basis:

Difficulties have been reported in relating glass composition to its short-term and long-term behavior. For example, SRL 165 glass has been observed to exhibit more durable behavior than PNL 76-68 glass when reacted in water, but the reverse is true in weathering tests (Abrajano et al., 1989). The explanation provided for this observation is that the composition of SRL 165 glass is more amenable to forming stable secondary phases that precipitate on the glass surface, keeping the solution concentrations of silica and other species low and, as a result, increasing the corrosion rate. The PNL 76-68 glass tends not to form such secondary phases in vapor hydration tests and, therefore, reacts more slowly than the SRL 165 glass

in such tests. Similar switching of durabilities of glasses of other compositions in saturated and unsaturated environments may arise when comparing short-term test data to long-term corrosion under a repository environment.

Recommendation:

Develop a better understanding of mechanisms that govern glass corrosion as a function of composition, amount of water in contact, and the duration of water contact. Quantify the reaction kinetics for West Valley and Savannah River glass compositions. Such information is needed for developing performance models that may be used for licensing of a repository.

Reference:

Abrajano, T.A., J.K. Bates, and J.J. Mazer. 1989. Aqueous corrosion of natural and nuclear waste glasses: II. Mechanisms of vapor hydration of nuclear waste glasses. *Journal of Non-Crystalline Solids* 108: 269-288.

Section 3.3.1 General Overview

COMMENT 13

Although there are numerous experimental studies of the release rates of radionuclides from waste forms, including comparisons with actinide solubilities of discrete phases (Bradley et al., 1979; Fillet et al., 1985; Grambow et al., 1991; Kerrisk, 1985; Schramke et al., 1985; Vernaz and Godon, 1991; Wilson and Bruton, 1991), only a few attempts have been made to incorporate these results into mechanistic models of glass corrosion. There is a concern that available experimental data may not be accurate enough or adequate for modeling of long-term glass performance.

Basis:

The Compendium states that, for mechanistic modeling, better quantified information is needed, especially in the areas of (i) solubilities of actinides as trace and minor components in the commonly formed clay, zeolite, and oxide alteration phases; (ii) stabilities and formation rates of colloids; (iii) stabilities of actinide complexes; and (iv) the sorption behavior of radionuclides onto mineral surface, including both colloids and alteration phases.

Recommendation:

Conduct appropriate experiments for generating data needed for developing models for predicting radionuclide releases from glass waste forms in a geologic environment.

References:

Bradley, D.J., C.O. Harvey, and R.P. Turcotte. 1979. *Leaching of Actinides and Technicium from Simulated High-Level Waste Glass*. PNL-3152. Richland, WA: Pacific Northwest Laboratories.

- Fillet, S., J.L. Nogues, E. Vernaz, and N. Jacquet-Francillon. 1985. Leaching actinides from the French LWR reference glass. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 50: 11-22.
- Grambow, B., R. Muller, A. Rother, and W. Lutze. 1991. Release of rare earth elements and uranium from glass in low pH high saline brines. *Radiochimica Acta* 52/53: 501-506.
- Kerrisk, J.F. 1985. Solubility limits and radionuclide dissolution. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 44: 237-244.
- Schramke, J.A., S.A. Simonson, and D.G. Coles. 1985. ^{237}Np and ^{239}Pu solution behavior during hydrothermal testing of simulated nuclear waste glass with basalt and steel. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 44: 343-350.
- Vernaz, E. Y., and N. Godon. 1991. Leaching of actinides from nuclear waste glass: French experience. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 257: 37-48.
- Wilson, C.N., and C.J. Bruton. 1991. Studies on spent fuel behavior under Yucca Mountain repository conditions. *Ceramic Transactions* 9: 423-441.
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- Section 3.3.2.1 Grambow Model
Section 3.3.2.2 Other Models Based on the Dissolution Control

COMMENT 14

The predictions of the models and the experimental data shown in Figures 3-9 and 3-10 are not particularly good even for a short-term test, leading to considerable doubt about the model's ability to predict long-term performance with any degree of confidence.

Basis:

The model shown in Figure 3-10 (i) appears to grossly underpredict silicon release—the main constituent of the waste glass, (ii) overpredicts uranium release by considerable amounts, (iii) does not appear to be as good as the Grambow Model (results shown in Figure 3-9), and (iv) considers only short-term experimental data, specifically, 28 d.

Recommendation:

Provide validation of the model with longer duration leaching tests.

Section 3.3.2.2.4 Effects of Secondary Phases

COMMENT 15

The secondary phases that form in glass corrosion tests or the rates at which they nucleate and grow cannot currently be predicted. Also, the reaction path programs can only predict the thermodynamically most stable phases (i.e., they rarely predict the phases actually observed in the tests). There is a concern related to current modeling procedures which exercise the models with only a restricted set of phases known to form in real systems (Grambow, 1987.)

Basis:

Current understanding of the reaction mechanisms involved in corrosion of glass is not considered adequate for predicting long-term performance.

Recommendation:

Further develop thermodynamic and kinetic data bases to validate the reaction mechanisms which form the basis of the performance models.

Reference:

Grambow, B. 1987. *Nuclear Waste Glass Dissolution: Mechanism, Model, and Application*. JSS Project—Phase IV. 87-02. Stockholm, Sweden: Nuclear Fuel and Waste Management Company.

Section 3.3.2.2.4 Secondary Phases

COMMENT 16

The tendency for partitioning into the surface layers of corroding glass is stronger for certain radionuclides (Buckwalter and Pederson, 1982; Petit et al., 1990). The concern is that the kinetics of partitioning are not well known, and also the effect of such partitioning on the long-term radionuclide release from the glass waste form has not been quantified.

Basis:

Partitioning may provide apparent short-term sequestering of certain radionuclides, giving the impression of retardation of the release by the waste form. However, the surface layers are unstable, and the occurrence of their spallation, though confirmed, is not always accurately predictable in time. This may lead to radionuclide release from the glass that is more characteristic of spike or step function releases that may violate the gradual release requirements of the regulations.

Recommendation:

More data and information on the solubilities of radionuclides in host mineral phases are needed to determine whether the radionuclides remain incorporated in the structure after the initially formed

amorphous phases transform into crystalline phases. Such information needs to be coupled with the stability characteristics of the alteration layers to develop models for predicting long-term releases of radionuclides.

References:

- Buckwalter, C.Q., and L.R. Pederson. 1982. Inhibition of nuclear waste glass leaching by chemisorption. *Journal of the American Ceramic Society* 65: 431-436.
- Petit, J.-C., G. Della Mea, J.-C. Dran, M.C. Magonthier, P.A. Mando, and A. Paccagnella. 1990. Hydrated layer formation during dissolution of complex silicate glasses and minerals. *Geochimica Cosmochimica Acta* 54: 1,941-1,955.
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Section 3.3.4 Linkage Between Models of Rate and Repository Performance Assessment Models

COMMENT 17

There is a concern that linkage between models for glass corrosion rate and repository performance assessment is inadequate.

Basis:

Current performance assessment strategies are usually probabilistically based and do not explicitly account for chemical and physical processes that will govern repository behavior (Liebetrau et al., 1987; McGrail and Engel, 1993; Shaw and McGuire, 1990). Efforts to perform deterministic performance assessment are far from being mature (Mouche and Vernaz, 1988; O'Connell and Drach, 1986). Most calculations to date have assumed glass corrosion rates that are either constant (Strachan et al., 1990; Umeki et al., 1986), a function of temperature (Chambre et al., 1988), solubility-controlled (National Academy of Sciences, 1983; Strachan et al., 1990), or controlled by external field mass transfer (Pigford and Chambre, 1985). The results of a performance assessment model that couples a Grambow-type glass dissolution model with a transport model, and incorporates the influence of other materials in the EBS (McGrail and Engel, 1993), show that models which assume solubility constraints on radionuclide concentrations may not be conservative. Experimental data for waste glass dissolution clearly show that measured actinide concentrations can be an order of magnitude higher than dissolved actinide concentrations due to formation of colloids containing actinides (Bates et al., 1992).

Recommendation:

More effort is needed to link glass corrosion rate models with the performance assessment models, with particular emphasis on including the contribution of actinides present in colloidal form.

References:

- Liebetrau, A.M., M.J. Apted, D.W. Engel, M.K. Altenhofen, C.R. Reid, D.M. Strachan, R.L. Erikson, and D.H. Alexander. 1987. AREST: A probabilistic source-term code for waste package

- performance analysis. *Waste Management '87*. La Grange Park, IL: American Nuclear Society: 535-544.
- McGrail, B.P., and D.W. Engel. 1993. Coupled process modeling and waste-package performance. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 294: 215-223.
- Shaw, R.A., and R.K. McGuire. 1990. *Demonstration of a Risk-Based Approach to High-Level Waste Repository Evaluation*. EPRI NP-7057. Palo Alto, CA: Electric Power Research Institute.
- Mouche, E., and E. Vernaz. 1988. Aqueous corrosion of the French LWR solution reference glass: First generation model. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 112: 703-712.
- O'Connell, W.J., and R.S. Drach. 1986. *Waste Package Performance Assessment: Deterministic System Model Program Scope and Specification*. UCRL-53761. Livermore, CA: Lawrence Livermore National Laboratory.
- Strachan, D.M., D.W. Engel, B.P. McGrail, P.W. Eslinger, and M.J. Apted. 1990. *Preliminary Assessment of the Controlled Release of Radionuclides from Waste Packages Containing Borosilicate Waste Glass*. PNL-7591. Richland, WA: Pacific Northwest Laboratory.
- Umeki, H., A. Suzuki, and R. Kiyose. 1986. A leach model for safety assessment. *Advanced Ceramics* 20: 523-529.
- Chambre, P.L., C.H. Kang, W.W. Lee, and T.H. Pigford. 1988. The role of chemical reaction in waste-form performance. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 112: 285-291.
- National Academy of Sciences. 1983. *A Study of the Isolation System for Geologic Disposal of Radioactive Waste*. Washington, DC: National Academy Press.
- Pigford, T.H., and P.L. Chambre. 1985. *Reliable Predictions of Waste Performance in a Geologic Repository*. LBL-20166. Berkeley, CA: Lawrence Berkeley Laboratory.
- Bates, J.K., W.L. Ebert, X. Feng, and W.L. Bourcier. 1992. Issues affecting the prediction of glass reactivity in an unsaturated environment. *Journal of Nuclear Materials* 190: 198-227.

Section 2.1.2.2.1 Crystallization

COMMENT 18

There is a concern that there could be a substantial increase in the devitrification of glass after fabrication, namely, during its storage or after emplacement in the repository. Increased devitrification could lead to unpredicted long-term performance, including an increase in the leaching rate.

Basis:

Since silicate glasses are thermodynamically unstable, there is a concern related to their long-term phase transformations outside the range of laboratory test time frames. Devitrification of a large volume of glass into crystalline phases could be detrimental to the repository performance. Investigations in this area have been limited to only short-term annealing treatments at temperatures below the glass transition temperature (Malow, 1989; Palmiter et al., 1991).

Recommendation:

Conduct longer-term isothermal annealing studies, at temperatures appropriate for the early repository isolation times, to understand and determine the kinetics of LTD.

References:

- Malow, G. 1989. Thermal and radiation effects in the range of the glass transition temperature T_g . *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 127: 153-162.
- Palmiter, T.V., I. Joseph, L.D. Pye. 1991. Effects of heat treatment on the microstructure of a fully simulated nuclear waste glass. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 212: 153-158.

Section 3.3.2.2.2 Other Models Based on Dissolution Control

COMMENT 19

The significance of conducting a flow-through test at 150 °C is unclear (Figure 3-10).

Basis:

The elevation at the Yucca Mountain repository site and the unsaturated nature of the site will not allow liquid phase water to exist at temperatures above 96 °C. The glass corrosion mechanism has been known to be influenced by the temperature at which the glass is reacted (Manaktala, 1992; Vernaz et al., 1988). Therefore, tests at 150 °C may not be relevant to the corrosion mechanism operative at the Yucca Mountain site.

Recommendation:

Justify the use of 150 °C data and provide comparison of results of tests conducted at 150 °C and at temperatures below the boiling point (e.g., 95 °C).

References:

- Manaktala, H.K. 1992. An Assessment of Borosilicate Glass as a High-Level Waste Form. CNWRA 92-017. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.

Vernaz, E.Y., J.L. Dussossoy, and S. Fillet. 1988. Temperature dependence of R7T7 nuclear waste glass alteration mechanisms. *Proceedings of the Materials Research Society Symposium*. Pittsburgh, PA: Materials Research Society: 112: 555-563.

3.2 QUESTIONS

Section 1.2.4 Significance of Glass Corrosion and Radionuclide Release Rate Data

QUESTION 1

What is the significance of the experimental observation reported in Figure 1-4 (Vernaz and Dussossoy, 1992) that shows that the RFs for all radionuclides investigated, namely U, ^{237}Np , ^{238}Pu , ^{239}Pu , and ^{241}Am , remain constant over the entire duration of the test (~ 380 d)? Is a 1-d test sufficient to determine RFs precisely? What are the factors that influence RFs?

Basis:

The understanding of the factors that influence the RF could provide a basis for glass composition optimization for Stage 3 performance.

Recommendation:

Provide detailed explanations of factors governing RFs (e.g., glass composition, test temperature, leachate composition, pH, reaction progress, etc.)

Reference:

Vernaz, E.Y., and J.L. Dussossoy. 1992. Current knowledge of nuclear waste glass dissolution mechanisms: The case of R7T7 glass. *Applied Geochemistry, Supplemental Issue 1*: 13-22.

Section 2.1.1 Waste Glass Compositions

QUESTION 2

The Compendium provides the compositions of four batches of reference DWPF glasses and a target composition of DWPF glass (Tables 2-1 and 2-2) (Westinghouse Savannah River Company, 1992). The target composition for the West Valley Demonstration Project (WVDP) glass is also provided along with compositions of four waste streams (Tables 2-3 and 2-4) (West Valley Nuclear Services Company, 1991). Will the glasses of different compositions be kept separated in a repository? Will the DWPF target glass bound the performance of four reference DWPF glass compositions or will different long-term performance credit be assigned to different glass compositions?

Basis:

Wide variations in the glass compositions could reduce the flexibility in emplacement of the vitrified wastes in a repository (assuming different compositions have different long-term performance).

Recommendation:

Provide the basis for five different compositions for DWPF glass. Also, provide the basis for the composition for WVDP blend glass (e.g., ease of processing, durability, etc.). Provide information on plans, if any, for reworking the already fabricated glass logs if their performance is found unacceptable for the chosen geologic repository.

References:

Westinghouse Savannah River Company. 1992. *Defense Waste Processing Facility Waste Form Compliance Plan*. WSRC-SW4-6, Rev. 1A. Aiken, SC: Westinghouse Savannah River Company.

West Valley Nuclear Services Company. 1991. *Waste Form Compliance Plan for the West Valley Demonstration Project High-Level Waste Form*. WVNS-WCP-001, Rev. 3. West Valley, NY: West Valley Nuclear Services Company.

Section 2.1.1 Waste Glass Compositions

QUESTION 3

The Compendium states that the composition(s) for the borosilicate glass for the United States program has not been defined as yet. When will it be defined, and what will be the basis? How many compositions of glass will be produced? Will the composition of Hanford glass be bound by the Savannah River or West Valley glass compositions?

Basis:

The decision regarding glass composition(s) needs to be made soon, that is, prior to the startup of the glass log production at West Valley and at Savannah River.

Recommendation:

Provide the basis on which glass composition(s) will be established for each of the three sites.

Section 3.3.2.2.2 Other Models Based on Dissolution Control

QUESTION 4

The experimentally observed release trends are reported to be reproduced by the model and the solution concentrations calculated to within a factor of two of the measured values (Figure 3-10). What are expected correlations between the experimental data and model for longer-term exposures?

Basis:

The correlation between the model predicted values and experimentally observed values for solution concentrations is not considered particularly strong. The basis of comparison is a very short-term test, namely, 28 days. The solution concentrations are very small, and the contribution of the back-reaction may have been small.

Recommendation:

Provide longer-term leaching data to judge the ability of the model to predict releases from the glass waste form.

4 SUMMARY

The Compendium provides a very broad and comprehensive coverage of the performance of borosilicate glass when exposed to an aqueous environment. Based on the information in the Compendium, it appears that there is insufficient understanding of the long-term performance of the glass waste forms. In addition, experimental data in a number of areas, needed to support or develop long-term performance assessment models, are still unavailable. These areas are:

- Glass corrosion kinetics in Stage 3 (beyond the laboratory testing time frame)
- Effects of the composition of glass on its long-term performance
- Data on the influence of EBS and repository construction materials on the acceleration of glass corrosion
- Devitrification kinetics at temperatures below glass transition temperature
- Thermodynamic properties of the stable and metastable phases formed in altered surface layers
- Incorporation into the glass performance models of release of radionuclides via colloids
- Linkage between models for glass corrosion rate and repository performance

The conclusion is that, at present, a model that can predict the long-term performance of glass waste forms with a high degree of confidence and precision is not available. However, there are several ongoing investigations and analytical efforts that may provide understanding of the long-term performance of glass waste forms and the necessary data for developing performance assessment models for licensing vitrified waste forms for geologic disposal.