CNWRA 92-017

AN ASSESSMENT OF BOROSILICATE GLASS AS A HIGH-LEVEL WASTE FORM

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ABSTRACT

This report provides an overview of the technical information related to a type of vitrified wasteform, namely borosilicate glass, for incorporating high-level reprocessing waste (HLW) from the nuclear fuel cycle. In the U.S. program, most of this waste results from defense activities of the government. Only a minor fraction results from a pilot study of commercial spent fuel reprocessing. (The report does not cover the subject of spent nuclear fuels from commercial reactors, which are also technically considered as HLW). The discussion covers the background leading to the choice of this wasteform over others; its typical composition, physical, chemical, and mechanical properties; alteration in characteristics as a result of fabrication processes and interim storage; and degradation modes in aqueous environments. Technical issues related to the geological disposal of borosilicate wasteforms have also been enumerated. No judgments regarding the licensability of borosilicate glass wasteform for geologic disposal under the federal regulations as stated in Title 10 Code of Federal Regulations Part 60 are made.

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1 INTRODUCTION

The nuclear fuel cycle is the primary source of high-level radioactive wastes (HLW). The term, nuclear fuel cycle, is a generic term for various support activities essential for the operation of commercial nuclear reactors, for the operation of defense and propulsion reactors, and for the production of weapon-grade materials from the defense reactors. Different types of operations exist within the fuel cycle leading to several waste streams, mainly classified as uranium mining, mill processing, enrichment, fuel fabrication, reactor operation, and spent fuel reprocessing. This report is restricted to the reprocessing wastes arising from the operations involving extraction of usable uranium and plutonium for refabrication of commercial reactor fuels [currently not being pursued in the United States for economic reasons and lack of operating commercial light water reactor (LWR) spent-fuel reprocessing facilities] or for the production of weapons in support of defense activities of the U.S. government. The long-term disposal strategy for these wastes is to immobilize the radionuclide inventory by transforming the liquid wastes into a solid form prior to disposal. The spent fuel from commercial power reactors, also classified as a HLW, is planned to be disposed of as intact fuel assemblies or as consolidated fuel rods without reprocessing. This report addresses the borosilicate glass wasteform.

A major fraction of such HLW arises from the first-cycle solvent extraction of spent fuel reprocessing. Also included in HLW are concentrated liquid wastes from subsequent extraction cycles. These wastes contain most of the nonvolatile products, a small amount of uranium and plutonium, and a majority of the actinides formed by transmutation of the uranium and plutonium in the reactors. Currently, HLWs are stored as liquid and sludge (precipitate) in storage tanks in the United States. The inherent limitations of such storage is the potential for leakage. Conversion of these wastes to a stable solid form offers several possible advantages for ultimate waste disposal, for example, a reduction in waste volume, depending upon the process used, and a general simplification of long-range waste management problems. The principal locations of storage of HLW in the United States, as neutralized sludge, salt, and liquid, are Hanford Reservation in Richland, Washington; Savannah River Site in Aiken, South Carolina; and West Valley Site in West Valley, New York.

During the past two decades, a substantial amount of effort in the United States and abroad has been devoted to developing, characterizing, and evaluating the performance of a number of host matrix materials for incorporating HLW for isolation from the biosphere. The wasteforms that have been developed to a significant practical level can be broadly divided into three types: (i) amorphous glasses, (ii) crystalline ceramics (single/polyphase), and (iii) multibarrier arrangements, such as phases containing radionuclides being further encapsulated in nonradioactive phases (e.g., coated particles or glass spheres encapsulated in metal matrices). Major programs related to types (ii) and (iii) ended in the United States as a result of the decision by the U.S. Department of Energy (DOE) to solidify the defense wastes in borosilicate glass. This decision was based in part on the recommendation of a DOE review panel. The rankings of candidate host matrices for HLW evaluated by the panel and other groups identified borosilicate as the first choice (Tang and Saling, 1990).

The scope of this report is limited to the review of selected properties and performance characteristics of the typical borosilicate glass wasteform. The intent is to provide a broad overview of the characteristics that may influence its performance in a geological repository and to list and discuss areas that have not been adequately investigated. However, this report is not a critical assessment of the borosilicate glass containing HLW from the point of its licensability for geological disposal under the federal regulations stated in Title 10 Code of Federal Regulations Part 60 (NRC, 1992).

2 BOROSILICATE GLASS AS A HIGH-LEVEL WASTEFORM

The term **glass** is commonly used to mean the fusion product of inorganic materials which has been cooled to a rigid condition without crystallizing. Glasses are characterized by certain well-defined properties which are common to all of them and different from those of liquids and crystalline solids. The glasses lack the long-range periodic order of the constituent atoms characteristic of crystalline materials (i.e., unlike crystals, glasses do not have a sharp melting point and do not cleave in a preferred direction). However, like crystalline solids, they show elasticity, and like liquids, they flow under a shear stress. Also, glasses, like liquids, are isotropic, a property which enhances their value in a variety of applications, including their use as a wasteform for radioactive wastes.

2.1 GLASS FORMATION

Glass formation is a kinetically controlled process. Any liquid, in principle, can be transformed into glass if cooled sufficiently fast and brought below the transition temperature range. A desirable glass-forming material is, however, one with a very slow rate of crystallization as a function of cooling rate. With conventional rates of cooling, some melts produce glass more easily than others. These observations have led to the postulation of a number of relationships correlating the nature of the chemical bond and the geometrical shape of the groups involved with the ease of glass formation. Although these empirical relationships explain glass formation in many systems, a unified mechanism capable of explaining the phenomenon of glass formation has not been developed as yet.

A widely accepted explanation of glass formation is based on the Zachariasen's random network model. According to this explanation, the atoms in glass, as in crystals, must form extended three-dimensional networks. This is based on the fact that mechanical properties and density of an oxide glass are similar to those of the corresponding crystal, and as a result, it could be inferred that the interatomic distances and interatomic forces must also be similar. Zachariasen proposed a set of empirical rules which an oxide must satisfy if it is to be a glass-former. For a simple oxide of the general formula A_2O_n, these are: (i) no oxygen atom may be linked to more than two atoms of A; (ii) the number of oxygen atoms surrounding A must be small (probably three to four); (iii) the oxygen polyhedra share corners with each other, not edges or faces; and (iv) for a three-dimensional network, at least three corners of each polyhedra must be shared (Cooper, 1978). A number of the limitations of the Zachariasen hypothesis have been pointed out, and a modification of his rules and other hypotheses have been proposed. However, they do not explain glass formation to a significantly more satisfactory extent than Zachariasen's random network model.

2.2 GLASS-FORMERS

Of all the elements, only a few in Groups III, IV, and V in the periodic table can form glasses on their own. However, oxides of elements, such as boron, silicon, germanium, and phosphorus, namely, B_2O_3, SiO_2, GeO_2, and P_2O_5, readily form glasses on their own and are commonly known as "glass-formers." These oxides are the main constituents of several mixed-oxide glasses. Oxides, such as As_2O_3 and Sb_2O_3, can also produce glass when cooled very rapidly (faster than conventional cooling), while other oxides, such as TeO_2, SeO_2, MoO_3, WO_3, Bi_2O_3, Al_2O_3, Ga_2O_3, TiO_2, and V_2O_5, will not form glass on their own but only upon melting with a suitable quantity of a second oxide. Figure 2-1 (Paul, 1990) shows a section of the periodic table with circled elements that have simple glass-forming oxides, and boxed elements that have oxides which are conditional glass-formers.

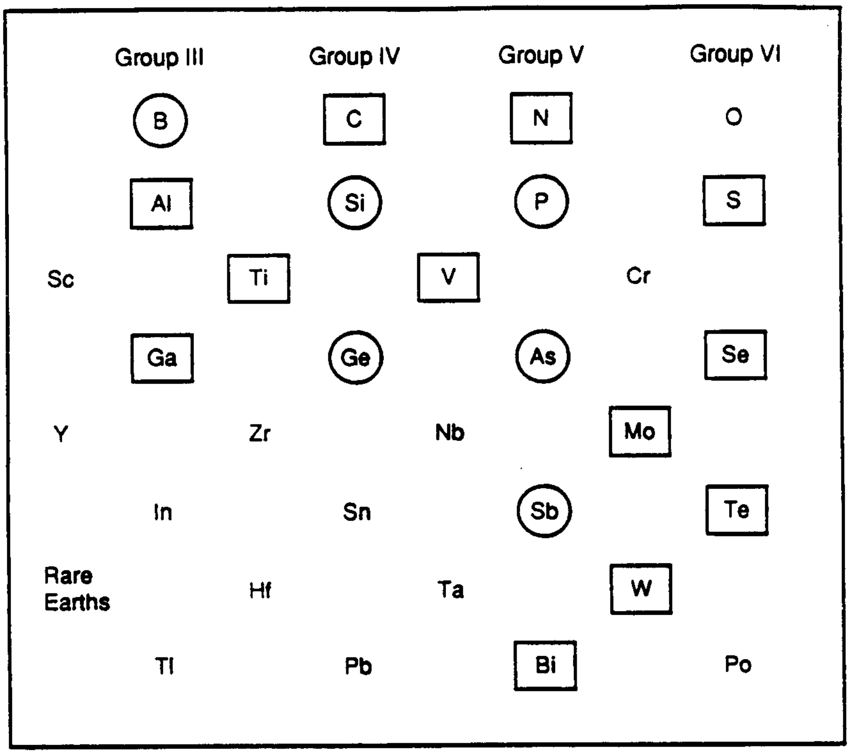


Figure 2-1. Oxides of Circled Elements are Glass-Formers; Oxides of Boxed Elements are Conditional Glass-Formers (Paul, 1990)

2.3 BOROSILICATE GLASS AS A HOST MATRIX

The major technical advantages of borosilicate glass as compared to other host matrices can be summarized as: (i) its ability to incorporate a wide variety of fission products and actinides, around thirty oxides that constitute the calcined wastes; (ii) its reasonably low formation temperature, below 1200°C; (iii) its ability to incorporate a high proportion of waste, up to 40 wt% depending upon the composition; (iv) its tolerance for reasonably wide variability in the waste composition; (v) its resistance to radiation-induced degradation; (vi) its ability to be produced remotely with a simple and reliable process requiring minimum maintenance; and (vii) its low susceptibility to leaching in an aqueous environment.

2.4 FABRICATION OF GLASS WASTEFORM

An HLW is produced by a process called vitrification. In this process, the waste slurry and the glass-forming compounds (frit) are continuously fed into a ceramic melter where the mixture is internally heated by electrodes, resulting in a homogeneous molten glass. The molten glass containing radioactive elements is then discharged into canisters (fabricated from type 304L stainless steel for the U.S. program) in the range of 1100 to 1200°C, where it solidifies upon cooling to below the glass transition temperature (T_g) in several hours to days. The precise cooling time depends on the pour canister dimensions, thickness, existence of any cooling fins, and the external cooling environment.

2.5 COMPOSITION AND RADIOACTIVE CHARACTERISTICS

Examples of borosilicate glass compositions for HLW are given in Tables 2-1 (Goldberg, 1990), 2-2 (Reimus et al., 1988), and 2-3 (Marra et al., 1992). Table 2-1 gives the composition for waste glass being considered for production by the Hanford Waste Vitrification Plant (HWVP), while Table 2-2 shows composition of two West Valley reference glasses. The projected composition of seven glasses from the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) are given in Table 2-3. The isotopes in HLW that constitute the main radiation hazard are listed in Table 2-4 (Tsoulfanidis and Cochran, 1991). The last three isotopes of Table 2-4 arise from irradiated steel components. The others are produced in UO_2 fuel either as fission products or as a result of neutron absorption and radioactive decay. In a mixture of radioisotopes in which many different half-lives are involved, the importance of isotopes changes, in terms of hazard, over time as shown schematically in Figure 2-2 (Tsoulfanidis and Cochran, 1991). The figure shows that, after 2,000 years, the toxicity of the waste becomes less than the toxicity of natural uranium.

Table 2-1. Composition of HWVP Waste Product (Goldberg, 1990)

Compound	Wt% of Compound	Element/ Isotope	Atomic Percent
AgO	2.5E−03	Ag	4.0E−04
As_2O_3	1.1E−05	As	1.1E−06
Al_2O_3	2.3E+00	Al	4.5E−01
Am_2O_3	5.0E−03	Am241 Am242 Am243	3.7E−04 5.7E−07 6.6E−08
B_2O	1.1E+01	B	1.2E+01
BaO	1.0E−01	Ba	1.3E−02
BeO	2.5E−02	Be	2.0E−02
CaO	8.3E−01	Ca	2.9E−01
CdO	7.6E−01	Cd	1.2E−01
CeO	1.5E−01	Ce	1.9E−02
Cr_2O_3	1.3E−01	Cr	3.4E−02
Cs_2O	1.5E−01	Cs	2.1E−02
CuO	1.5E−01	Cu	3.7E−02
Dy_2O_3	2.6E−05	Dy	2.8E−06
Er_2O_3	7.7E−07	Er	8.0E−08

Table 2-1. Composition of HWVP Waste Product (Cont'd)

Compound	Wt% of Compound	Element/ Isotope	Atomic Percent
Eu_2O_3	5.0E−03	Eu	5.6E−04
F	3.0E−01	F	3.1E−01
Fe_2O_3	7.0E+00	Fe	1.7E+00
Gd_2O_3	2.5E−03	Gd	2.7E−04
GeO_2	3.9E−05	Ge	7.4E−06
Ho_2O_3	1.3E−06	Ho	1.4E−07
In_2O_3	3.3E−04	In	4.7E−05
K_2O	1.3E−02	K	2.7E−03
La_2O_3	7.3E−01	La	8.9E−02
Li_2O_3	3.7E+00	Li	2.4E+00
MgO	8.0E−01	Mg	3.9E−01
MnO	1.5E−01	Mn	4.2E−02
Mo_2O	3.0E−01	Mo	5.3E−02
Na_2O_3	1.1E+01	Na	7.0E+00
NbO	2.5E−03	Nb	4.2E−04
Nd_2O_3	3.9E−01	Nd	4.6E−02
NiO	5.8E−01	Ni	1.5E−01
NpO_2	2.5E−02	Np237	1.8E−03
P_2O_5	2.2E−01	P	6.2E−02
PbO_2	1.3E−02	Pb	1.1E−03
PdO	5.0E−02	Pd	8.1E−03
Pm_2O_3	2.5E−02	Pm	2.9E−03
Pr_2O_3	1.0E−01	Pr	1.2E−02
PuO_2	5.0E−03	Pu238 Pu239 Pu240 Pu242	6.6E−07 3.3E−04 3.6E−04 3.7E−04

Table 2-1. Composition of HWVP Waste Product (Cont'd)

Compound	Wt% of Compound	Element/ Isotope	Atomic Percent
Rb_2O_3	5.0E−02	Rb	9.1E−03
Rh_2O_3	5.0E−02	Rh	7.8E−03
Ru_2O_3	1.5E−01	Ru	2.4E−02
SO_3	1.6E−01	S	4.0E−02
Sb_2O_3	1.5E−03	Sb	2.0E−04
SeO_2	7.6E−03	Se	1.4E−03
SiO_2	5.4E+01	Si	1.8E+01
Sm_2O_3	5.0E−02	Sm	5.7E−03
SnO	1.0E−02	Sn	1.5E−03
SrO	1.0E−01	Sr	1.9E−02
Ta_2O_5	7.6E−03	Ta	6.8E−04
Tb_2O_3	5.6E−05	Tb	6.1E−06
Tc_2O_7	1.0E−01	Tc	1.3E−02
TeO_2	2.5E−02	Te	3.1E−03
TiO_2	2.5E−03	Ti	6.2E−04
Tm_2O_3	4.2E−11	Tm	4.4E−12
UO_8	1.2E+00	U234 U235 U236 U238	6.2E−06 7.4E−04 5.9E−05 8.9E−02
Y_2O_3	5.0E−02	Y	8.8E−03
ZrO_2	3.8E+00	Zr	6.1E−01
Atomic Percent of Oxygen = 5.6E+01			

Table 2-2. Composition of West Valley Reference Glasses (Reimus et al., 1988)

Oxides	Weight Percent	
	DG-WV1; WVCM-47	DG-WV30; WVCM-50
Al_2O_3	8.05	9.86
B_2O_3	12.08	12.27
BaO	0.05	0.19
CaO	0.60	0.82
CeO_2	0.07	0.72
Cr_2O_3	0.20	0.14
Cs_2O	0.08	0.07
CuO	0.00	0.04
Fe_2O_3	12.20	11.93
K_2O	1.29	1.61
La_2O_3	0.03	0.04
Li_2O	2.03	2.22
MgO	1.33	0.79
MnO_2	1.31	1.21
MoO_3	0.01	0.04
Na_2O	9.27	9.79
Nd_2O_3	0.12	0.14
NiO	0.28	0.31
P_2O_5	2.52	2.47
PdO_2	0.00	0.00
Pr_6O_{11}	0.03	0.04
RhO_2	0.00	0.00
RuO_2	0.00	0.00
SiO_2	42.59	39.60
Sm_2O_3	0.03	0.02
SO_3	0.30	0.23
SrO	0.03	0.02
ThO_2	3.61	3.52
TiO_2	0.99	0.84
UO_2	0.56	0.61
Y_2O_3	0.02	0.02
ZnO_2	0.00	0.03
ZrO_2	0.29	0.40
Total	99.97	99.99

Table 2-3. Projected Compositions DWPF HLW Glasses (adapted from Marra et al., 1992)

Glass Components Wt%	Blend	HM	Purex	#1	#2	#3	#4
Al_2O_3	4.16	7.15	2.99	4.88	4.63	3.44	3.43
B_2O_3	8.05	7.03	10.33	7.78	7.88	7.69	8.14
BaO	0.18	0.11	0.20	0.15	0.16	0.18	0.25
CaO	1.03	1.01	1.09	1.22	1.08	0.99	0.84
Cr_2O_3	0.13	0.09	0.15	0.11	0.13	0.14	0.14
Ca_2O	0.08	0.06	0.06	0.06	0.02	0.06	0.09
CuO	0.44	0.25	0.42	0.40	0.42	0.40	0.45
Fe_2O_3	10.91	7.78	13.25	12.84	11.12	11.71	11.71
K_2O	3.68	2.21	3.41	3.33	3.38	3.40	3.86
Li_2O	4.44	4.62	3.22	4.43	4.50	4.51	4.29
MgO	1.41	1.49	1.41	1.42	1.42	1.42	1.43
MnO_2	2.05	2.15	2.07	2.11	1.73	1.87	3.11
MoO_3	0.15	0.22	0.08	0.11	0.17	0.12	0.20
Na_2O	9.13	8.56	12.62	9.00	9.21	9.01	9.16
Nd_2O_3	0.22	0.55	0.06	0.15	0.26	0.17	0.39
NiO	0.89	0.41	1.19	0.75	0.90	1.05	1.06
RuO_2	0.03	0.04	0.01	0.02	0.04	0.03	0.05
SiO_2	51.9	55.8	46.5	50.2	52.1	52.6	50.1
TiO_2	0.89	0.56	0.68	0.68	0.69	0.68	1.03
ZrO_2	0.14	0.33	0.05	0.10	0.17	0.12	0.22
Total	99.91	100.42	99.79	99.74	100.01	99.59	99.95

Table 2-4. Important Isotopes Encountered in Radioactive Wastes (adapted from Tsoulfanidis and Cochran, 1991)

Isotope	Half-Life (yr)	Radiation of Primary Concern
^{90}Sr	29	Beta particles
^{129}I	1.6×10^7	Beta particles
^{135}Cs	2.0×10^6	Beta and gamma particles
^{137}Cs	30	Beta and gamma particles
^{99}Tc	2.0×10^5	Beta particles
^{229}Th	7.3×10^3	Alpha particles
^{230}Th	7.7×10^4	Alpha particles
^{237}Np	2.1×10^6	Alpha particles
^{239}Pu	2.4×10^4	Alpha particles
^{240}Pu	6.6×10^3	Alpha particles
^{241}Am	460	Alpha particles
^{243}Am	7.4×10^3	Alpha particles
^{243}Cm	32	Alpha particles
^{244}Cm	18	Alpha particles
^{59}Ni	8.0×10^4	X rays
^{94}Nb	2.0×10^4	Beta and gamma particles
^{60}Co	5.3	Gamma particles

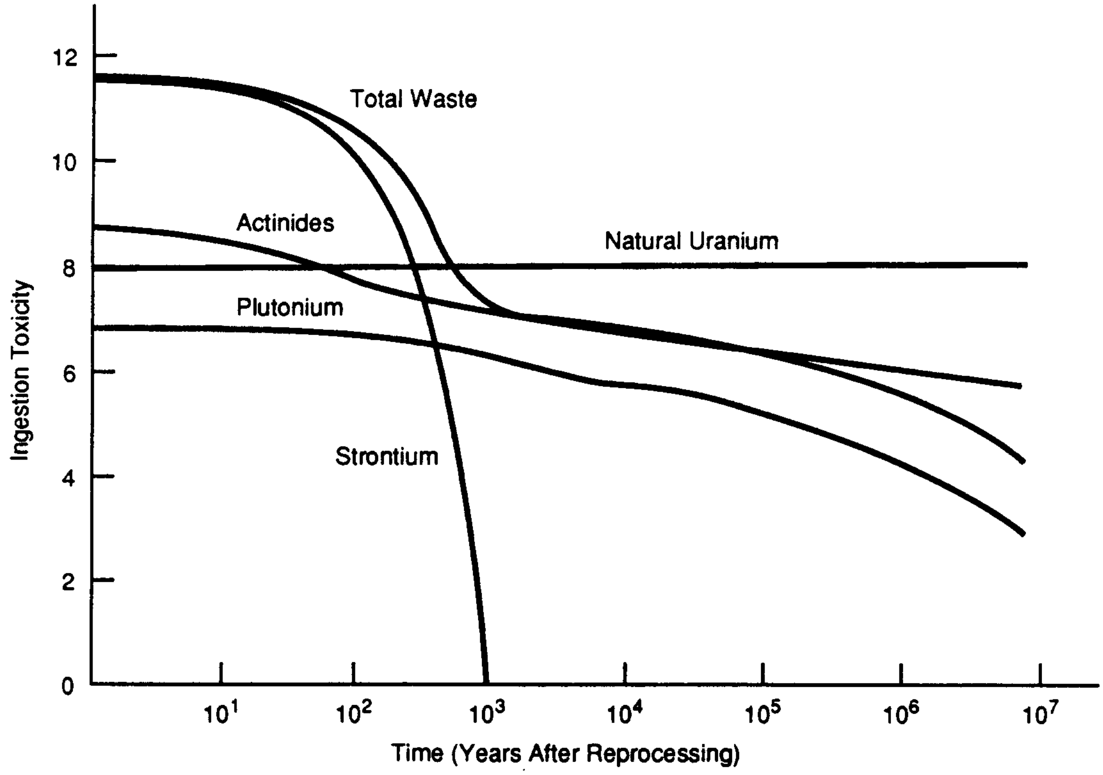


Figure 2-2. Decrease in Ingestion Toxicity of Radioactive Wastes as a Function of Time (Tsoulfanidis and Cochran, 1991)

3 PROPERTIES OF BOROSILICATE GLASS

3.1 CHEMICAL COMPOSITION

3.1.1 Frit Composition

Numerous waste-free glasses (frits) have been investigated in terms of processing temperatures, waste loadings, and product quality. However, only a few are being considered for use or are used on a large scale. The chemical compositions of typical frits for HLW are listed in Table 3-1 (adapted from Lutze and Ewing, 1988). The frit labeled AVM is composed only of the ternary system Na_2O-B_2O_3-SiO_2 components, the basic glass system for most HLW wasteforms. The other fission-product-free base glasses (frits) contain one or more other components in addition to silica, boron oxide, and sodium oxide. The reasons for adding those components are discussed in the following sections.

Table 3-1. Typical Compositions of Selected Glass Frits (adapted from Lutze and Ewing, 1988)

Component Identification	Composition in Weight Percent									
	SRL 165	SON 68	SM 513	PNL 76-68	UP 209	GP 98/12	P 0422	SM 539	AVM	SRL 131
SiO_2	68.0	54.9	58.6	59.4	68.5	58.5	61.0	45.5	56.1	58.7
B_2O_3	10.0	16.9	14.7	14.3	15.0	11.0	19.9	33.0	25.3	14.9
Li_2O	7.0	2.4	4.7	-	5.4	-	4.3	4.5	-	5.8
Na_2O	13.0	11.9	6.5	11.3	11.2	17.5	1.4	10.5	18.6	18.0
K_2O	-	-	-	-	-	-	2.8	-	-	-
TiO_2	-	-	5.1	4.5	-	3.6	-	-	-	1.04
CaO	-	4.9	5.1	2.9	-	4.5	2.8	6.5	-	-
MgO	1.0	-	2.3	-	-	3.3	-	-	-	2.1
Al_2O_3	-	5.9	3.0	-	-	1.6	5.0	-	-	-
ZnO	-	3.0	-	7.6	-	-	2.8	-	-	-
ZrO_2	1.0	-	-	-	-	-	-	-	-	0.45
La_2O_3	-	-	-	-	-	-	-	-	-	0.45

3.1.2 Wasteform Composition/Silicate Glass Systems

Ideally, the chemically most durable glass wasteform is vitreous silica (SiO_2) with a small amount of waste oxides dissolved in the SiO_2 network. However, a high silica wasteform is not practical due to the requirement of very high melting temperatures, typically $\geq$1700°C. At such temperatures, several high radioactivity fission products, including cesium, ruthenium, technetium, selenium, sulfur, and fluorine will volatilize instead of being incorporated into the glass matrix. Also, inactive constituents of the waste, such as alkali oxides, are volatile at these temperatures and will clog the off-gas system. Therefore, radioactive glass formation temperatures have to be in the much lower range of 1100°C and

1200°C. This requires the use of other glass-forming compounds to lower the melting temperature of the glass.

3.1.3 Manufacturing Considerations

For a particular radioactive waste composition and the processing technique, borosilicate glass composition most often reflects a compromise between chemical durability of the product, ease of manufacturing, and economic considerations. The frit composition is chosen so that the glass melt provides sufficient electrical conductivity for proper mixing of the wasteform constituents. The desirable electrical conductivity is attained generally by adding enough alkalis, typically sodium and lithium, to the glass-forming mixture. Potassium may also be used. Typical specific resistance values for the glass melt range between 1 and 10 ohm-cm (Plodinec and Wiley, 1979). Although this manufacturing criterion for glass frit is easily met, a suitable glass composition may still be difficult to find due to additional composition constraints imposed by the waste oxides to be incorporated in the wasteform. For example, sodium is a typical, sometimes dominating constituent of HLW streams with concentrations which can range of up to 30 wt% of the dry waste. This requires the adjustment of alkali content of the frit to account for the alkali concentration in the waste. Other nonradioactive constituents in the waste at relatively high concentrations (e.g., iron and aluminum) also require adjustment of the glass composition. High loadings of certain other elements/compounds may require special glass frit compositions to meet the viscosity and electrical resistivity requirements imposed by the manufacturing process.

Both sodium and lithium have a strong influence on the viscosity of the melt. Lithium is not contained in HLW streams, but is a typical constituent of the frit. This alkali is added for several reasons. Lithium, a network modifier, can effectively decrease the formation temperature and the specific electrical resistance of the glass melt (Mellinger and Chick, 1979). About half as much of lithium oxide as sodium oxide (in wt%) is required to achieve a comparable effect in lowering the formation temperature and the specific resistivity of the melt. Depending on the molar ratio, the use of sodium and lithium together can be even more effective than either of these compounds individually because of the well-known mixed-alkali effect.

Typical viscosity values range between 50 and 120 dPa.s at 1150°C, but may be lower in some cases. Lower viscosities of the glass melt in the furnace facilitates homogenization of the constituents. However, very low viscosities may make the pouring of the molten glass in the metallic container more difficult to control. The results of the resistance and viscosity measurements indicate a change in one of these properties alone cannot be made by controlling the alkali concentration (Schiewer, 1986). Hence, changes in viscosity, independent of resistivity, have to be made by the addition of other elements to the melt. The five predominantly used additives are: Al, Ca, Mg, Zn, and Ti. These elements are added in the form of oxides. Their roles are described in the following sections.

3.1.3.1 Al_2O_3

Aluminum is a network former at low concentrations and occurs as AlO_4 tetrahedra in the glass structure. This structural unit increases the chemical durability of the glass. On the other hand, addition of aluminum also leads to an increase in the viscosity of the glass melt and of possibly producing inhomogeneous glass (Plodinec and Wiley, 1979). The general effect of the increase of the alumina, Al_2O_3, content is similar to decreasing the total alkali oxide content. However, high additions of aluminum may increase the susceptibility of the glass to devitrification. Some of the devitrification products, such as nepheline, $KNa_3Al_4Si_4O_{16}$, are fairly soluble in water.

3.1.3.2 CaO, MgO, and ZnO

The three elements, Ca, Mg, and Zn, increase the chemical durability of the glass through stabilization of the glass structure. These three elements are also known to increase the viscosity in alkali silicate glasses at low temperatures (400°C to 600°C range) and decrease it at high temperatures (1000°C to 1300°C range) (Gehlhoff and Thomas, 1926). The influence of magnesium varies strongly with glass composition. Depending on the amount, substitution of CaO by MgO can lead to a pronounced viscosity minima (Turcotte and Wald, 1978). At higher concentrations (e.g., 20 wt%), ZnO can lead to devitrification of the glass-leading to the formation of willemite, Zn_2SiO_4. The PNL 72-68 borosilicate glass (composition given in Turcotte and Wald, 1978) is a typical example of a high-zinc glass (21.3 wt% ZnO). At a waste loading of 20 wt%, about 14 wt% of willemite reportedly formed upon annealing the glass at 600°C after one year (Turcotte and Wald, 1978).

3.1.3.3 TiO_2

Titanium is a network former in silicate glasses. TiO_4 tetrahedra form the structural unit. A decrease in viscosity for waste glass melts can be achieved by increasing the TiO_2 content of the wasteform. However, larger additions of titanium may lead to TiO_2 particles becoming active as a nucleating agent for crystalline phases such as ferrite, $Fe_2O_4M^{II}$, and eucryptite, $LiAlSiO_4$, (Plodinec, 1979, 1980) and could also be incorporated as a constituent of crystalline phases like titanite (sphere), $CaTiSiO_5$, and rutile, TiO_2 (Schiewer, 1986).

3.1.4 Relationship Between Composition and Wasteform Processing

A model for predicting property response as a function of glass composition has been developed through a statistical study (Chick et al., 1980). The major properties investigated in the development of the model included viscosity, specific resistance, and volatility of the glass melts. Figure 3-1 (Plodinec and Wiley, 1979), developed on the basis of the study, shows the effect of various glass component concentrations on volatility. For example, increasing contents of alumina, Al_2O_3, and/or silica, SiO_2, to the glass melt decreased the volatility relative to a reference (centroid) composition. However, the volatility increased with the addition of calcium oxide, CaO; disodium monoxide, Na_2O; and boric oxide, B_2O_3. The measured mass losses showed the expected trends: the most volatile constituents were sodium and boron, probably as oxides. The effect of increase in SiO_2 and Al_2O_3 content was to reduce the volatility, because these components made the more volatile constituents less mobile in the melt. Similarly, Figure 3-2 (Plodinec and Wiley, 1926) shows the effect of various glass component concentrations on viscosity of the melts. As expected, qualitatively the trends are reversed (i.e., increase in viscosity led to a decrease in volatility and vice versa). The effect of chromium on viscosity has been explained by the formation of crystalline chromium mineral phases which formed in air-quenched melts. These crystals provide additional friction upon shear movement in the melt (i.e., increase the viscosity of the melt). The potential use of a statistical model lies in the quantitative prediction of product properties. However, its use outside the narrow composition field of the wasteform studied may not be valid. Such a statistical approach to optimize the borosilicate glass composition has been used for the

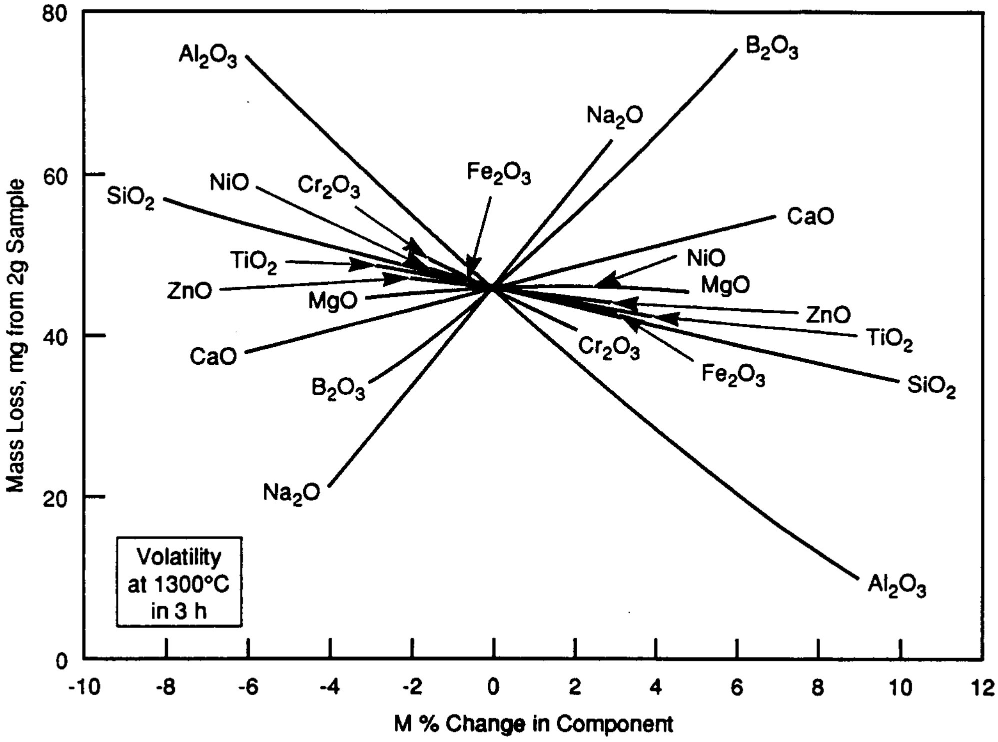


Figure 3-1. Effect of Component Concentration on Volatility (adapted from Plodinec and Wiley, 1979)

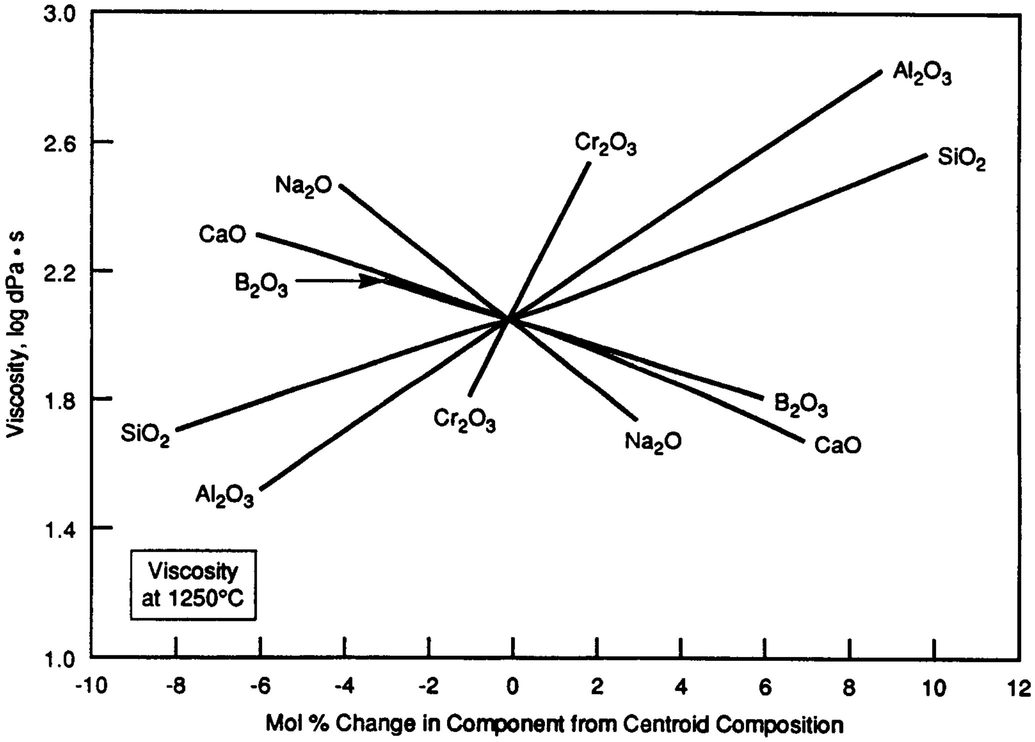


Figure 3-2. Effect of Component Concentration on Viscosity (adapted from Plodinec and Wiley, 1979)

processing of HLW generated in the U.S. from the reprocessing of spent LWR fuels from commercial nuclear reactors (Turcotte and Wald, 1978).

3.1.5 Structure of Borosilicate Glass Wasteform

Borosilicate glass is a noncrystalline (amorphous) product formed by the fusion of oxides of radioactive elements with suitable fluxing agents (frit). The overall formulation is a mixture of glass formers, modifiers, and intermediates with the HLW oxides. The structural framework of the glass is provided primarily by the SiO_4 tetrahedra. Neighboring silicate tetrahedra are bonded together by sharing strong ionic-covalent bridging oxygen bonds. Other multivalent species, such as B^{3+}, Fe^{2+}, Fe^{3+}, rare earths, or actinides are also generally bonded within the network by bridging oxygen bonds. Low-valence ions, such as Na^+, Cs^+, Sr^{2+}, etc., are bonded into the network by sharing various nonbridging oxygen bonds, depending upon the size of the ion. Radioactive waste is not only encapsulated by glass, but each waste atom is separately bound in the glass structure by a chemical bond. [There are certain minor exceptions (e.g., ruthenium and palladium remain as discrete particles encapsulated in the glassy matrix).] This difference in the type of bonding in the glass network is believed to be responsible for its complex leaching behavior in aqueous environments. Figure 3-3 (Hench et al., 1986) shows a schematic of an alkali borosilicate glass structure, in two dimensions, containing dissolved nuclear wastes.

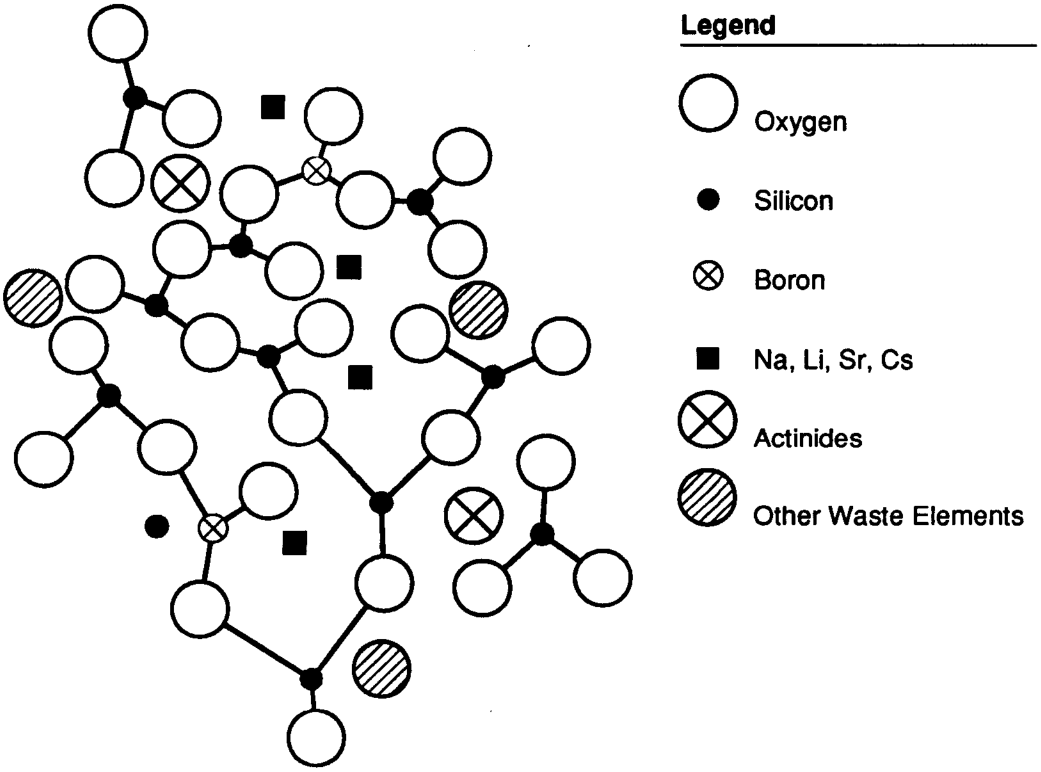


Figure 3-3. Schematic of Alkali Borosilicate Glass Structure Containing Dissolved Nuclear Wastes (adapted from Hench et al., 1986)

3.2 PHASE TRANSFORMATION

Two major types of phase transformations are observed in multicomponent glasses. These are: (i) devitrification or crystallization and (ii) liquid-liquid phase separation.

3.2.1 Devitrification

After glass melt is poured into a metallic canister at approximately 1150°C, the large mass of glass takes several hours to cool to below 400°C. It is during this period that crystallization or devitrification of the wasteform occurs. Cooling down through the 900°C to 600°C temperature range is considered the critical devitrification temperature zone for most compositions. Almost all glass compositions proposed for vitrification of HLW are expected to devitrify to some extent during fabrication into a solid monolith.

The devitrification or crystallization process involves transformation of the amorphous glass into more ordered crystalline phases. Many different crystalline phases have been reported in devitrified borosilicate glasses, spinel, [(Fe, Ni, Mn)Fe_2O_4], and acmite, $NaFeSi_2O_6$, being the predominant ones. These crystalline phases are chemically less durable. Decrease in the overall chemical durability of the glass of up to an order of magnitude, due to devitrification, have been reported. Crystallization kinetics from experimental time-temperature-transformation (TTT) curves, such as shown in Figure 3-4 (Bickford and Jantzen, 1986), can be used in quantifying the amount of devitrification in the wasteform monolith. (The amount of crystallization is related to the time the wasteform is within the nose of the transformation curve). The beginning of crystallization, at the nose of the curve in Figure 3-4 (Bickford and Jantzen,

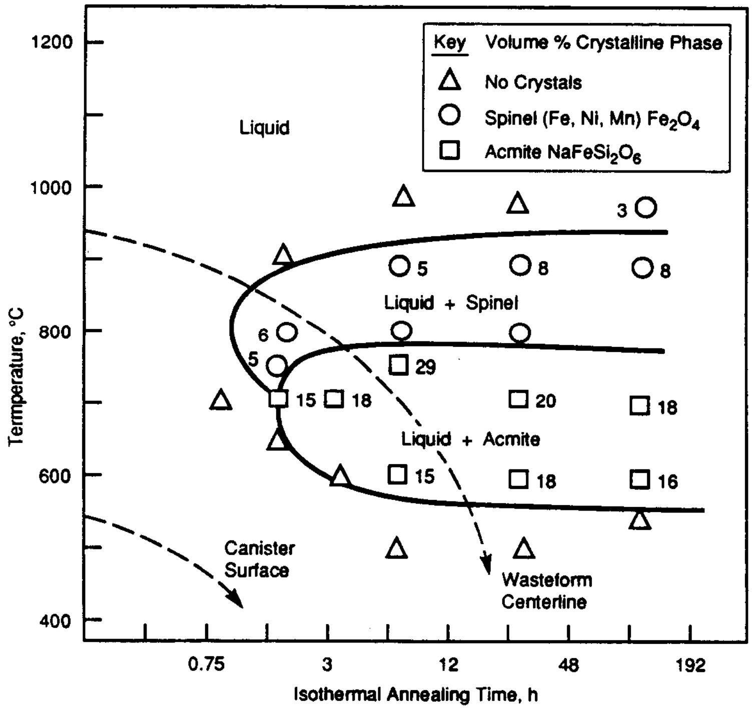


Figure 3-4. Time-Temperature-Transformation (TTT) Curves for SRL-165 Borosilicate Glass (adapted from Bickford and Jantzen, 1986)

1986) is shown to commence after about 45 minutes at 800°C. (However, the crystallization kinetics could be much faster or slower depending upon the composition and the size of the wasteform). This figure also suggests that crystallization in borosilicate glass is unlikely to occur or increase in the geological repository beyond the amount already present at the time of emplacement, as the repository temperature is expected to be below 300°C according to the present design considerations (U.S. DOE, 1988). An amount up to 10 vol% devitrification can occur during normal processing of the borosilicate glass wasteform (Bickford and Jantzen, 1984).

3.2.2 Crystalline Phases in Borosilicate Glass

Devitrification can have a number of deleterious effects on the integrity of the wasteform. The major effects are localized microcracking due to volume expansion of the crystalline phases and reduced overall chemical durability in an aqueous environment due to higher solubility of some of the crystalline phases. The crystalline phases that have been reported in borosilicate glasses as a result of devitrification include: trevorite, $NiFe_2O_4$; cerianite, CeO_2; willemite, Zn_2SiO_4; $SrMoO_4$ for PNL 72-68 glass; and trevorite, $NiFe_2O_4$; cerianite, CeO_2; trevorite, $NaFeSi_2O_6$, for 76-68 glass. In PNL 77-260 glass, the following phases have been detected: trevorite, $NiFe_2O_4$; cerianite, CeO_2; $GdTi_2O_7$; and $Ca_3Gd_7[SiO_4]_5(PO_4)O_2$. Pd and RuO_2 are present as insoluble element and compound, respectively (Turcotte et al., 1980). These two inclusions act as heterogeneous nuclei for the crystalline phases, with the general effects of accelerating the initiation of the devitrification process and controlling the size and morphology of the crystallites. The efficiency of RuO_2 as a nucleating agent is illustrated by the acceleration of the initiation of nucleation and crystallization in waste glass from 96 hours to 3 hours in a 600°C isothermal heat treatment (Jantzen and Plodinec, 1984; Jantzen et al., 1984).

Experiments have been performed both in air and in a reducing environment on SRL 165 glass to study its devitrification characteristics. The most abundant crystalline phases formed were spinel (various Fe, Mn, Cr, Ni compositions) and acmite as indicated in the TTT curves shown in Figure 3-4 (Bickford and Jantzen, 1986). The two distinct regions shown in Figure 3-4 with (glass+spinel) and (glass+acmite) present overlapped considerably when the samples were prepared and annealed in air, but were separated under reducing conditions as shown in Figures 3-5(A) and 3-5(B) (Jantzen et al., 1984). It was also reported that glasses prepared under normal oxygen partial pressure led to higher total yields of crystals than when they were prepared under reduced oxygen pressure (Jantzen and Plodinec, 1984; Jantzen et al., 1984). Oxygen pressure was also found to influence the composition of the crystalline phases, namely, with less oxygen present, spinels rich in iron and acmite and low in silicon were favored. It has been suggested that solubility and dispersion of nucleating agents (e.g., RuO_2) may be affected by oxygen pressure, which may influence the type of crystalline phases formed (Jantzen and Plodinec, 1984; Jantzen et al., 1984). Chromium appeared to be involved in spinel formation only at higher temperatures, 800°C to 900°C, while acmite nucleated heterogeneously in the temperature range of 650°C to 800°C. No crystallization was observed at temperatures of 500°C and below.

3.2.3 Noble Metal Precipitates

Most simulated nuclear waste glasses do not contain the fission products of noble metals, such as palladium, rhodium, and ruthenium and their alloys, although they are always present in liquid HLW and in dissolver residues. The crystallization behavior of glasses which do not contain these noble metals is likely to be different from radioactive glasses that do have these elements. For example, as discussed earlier, their presence in the glass melt can have a significant effect on crystallization, because a major

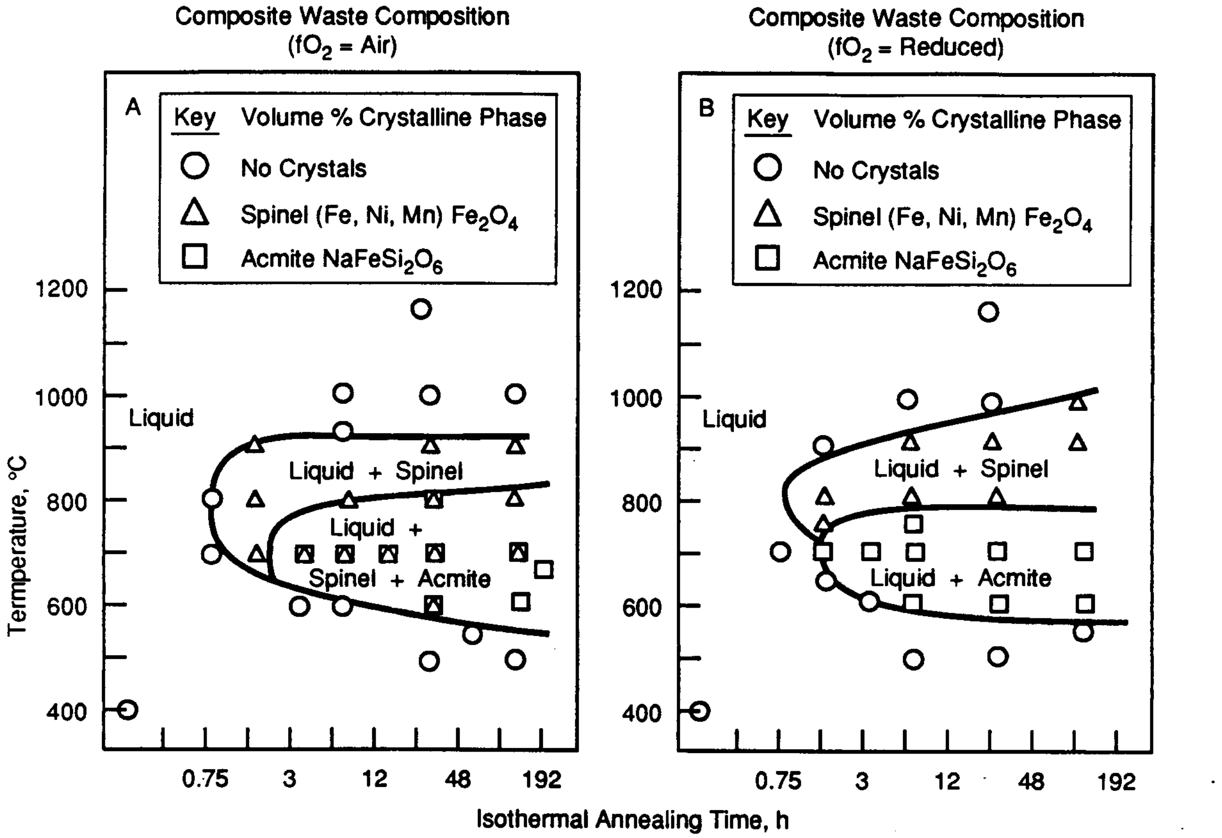


Figure 3-5. Time-Temperature-Transformation (TTT) Curves for SRL 165 Glass Made Under Oxidizing (A) and Reducing (B) Conditions (Jantzen et al., 1984)

fraction of these elements does not become part of the glass phase but appears as separate phases. Detailed studies related to the amount of noble metal oxides that are acceptable in the melt are part of the manufacturing process development programs. In a study on West Valley borosilicate glasses, it has been concluded that presence of up to 0.1 wt% total noble metal oxides does not significantly affect the glass durability as measured by aqueous leaching tests (Reimus et al., 1988).

3.2.4 Yellow Phase

Sulfur, in the form of thenardite (Na_2SO_4), SO_3, or SO_2+O_2, can be incorporated into the glass structure up to 1 wt%. Concentrations above this limit in the molten state lead to the formation of a second phase. A similar phenomenon has been observed with hexavalent molybdenum, molybdite (MoO_3), which has a solubility limit in borosilicate glass of approximately 1 wt%. The separated Mo-rich phase is sometimes referred to as the "yellow phase" because of its color. The crystalline products in the yellow phase are easily dissolved in water. Hence, the formation of a yellow phase leads to a reduced chemical durability of the wasteform. In analysis of the constituents of a yellow phase, the following compounds were identified: 51 wt% alkali sulfates, 5 wt% alkali chromates, 6 wt% alkali molybdates, 19 wt% $CaMoO_4$, 14 wt% $Ba(Sr)CrO_4$, and a few percent of unidentified phases (Schiewer et al., 1982). No data were reported on the partitioning of long-lived radionuclides, such as plutonium, neptunium, and technetium, between the glass and the yellow phase. The influence of the Mo^{3+}/Mo^{6+} ratio can be a critical factor in yellow-phase formation in glasses, because the oxidation of Mo^{3+} can reduce the solubility of molybdenum. The low solubility limit and the relatively high fission yield make molybdenum a critical element in the vitrification process. As a result, molybdenum concentration influences the limit of the waste loading in the glass.

3.2.5 Glass-in-Glass Phase Separation

Glass-in-glass phase separation has been observed in many nuclear waste glasses. Such a phase separation results from an immiscibility (liquid-liquid phase separation) at temperatures above the glass transition temperature. The phenomenon leads to the formation of a SiO_2-rich phase, resulting in depletion of the bulk of glass in SiO_2. This reduces the chemical durability of the wasteform. Addition of carbon to the melt is known to reduce the degree of such phase separation in the bulk. The glass-in-glass phase separation phenomena encountered in the quaternary system, Na_2O-B_2O_3-SiO_2-X (X is a fourth component or the sum of several components), has been reported in the literature (Schiewer, 1986). The composition diagram is shown schematically in a tetrahedron in Figure 3-6 (Schiewer, 1986), together with a projection of the X = 20 wt% plane onto the plane of the ternary system, Na_2O-B_2O_3-SiO_2. In the quaternary system, the concentration ranges between 40 and 80 wt% SiO_2, 5 to 30 wt% B_2O_3, Na_2O, and X are most relevant for borosilicate glass wasteforms. The projection of the immiscibility limit at 7.5 wt% Na_2O in the X = 20 wt% plane is at 9.2 percent in the Na_2O-B_2O_3-SiO_2 plane. The shaded Region I in Figure 3-6 (Schiewer, 1986) exhibits the immiscibility gap at 600°C (i.e., glass compositions within

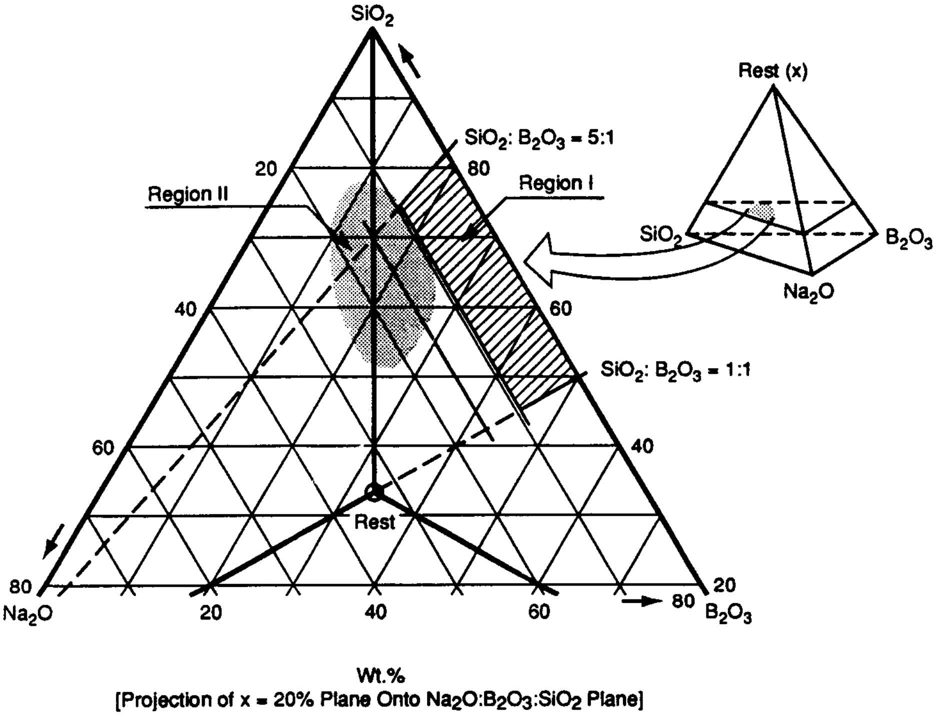
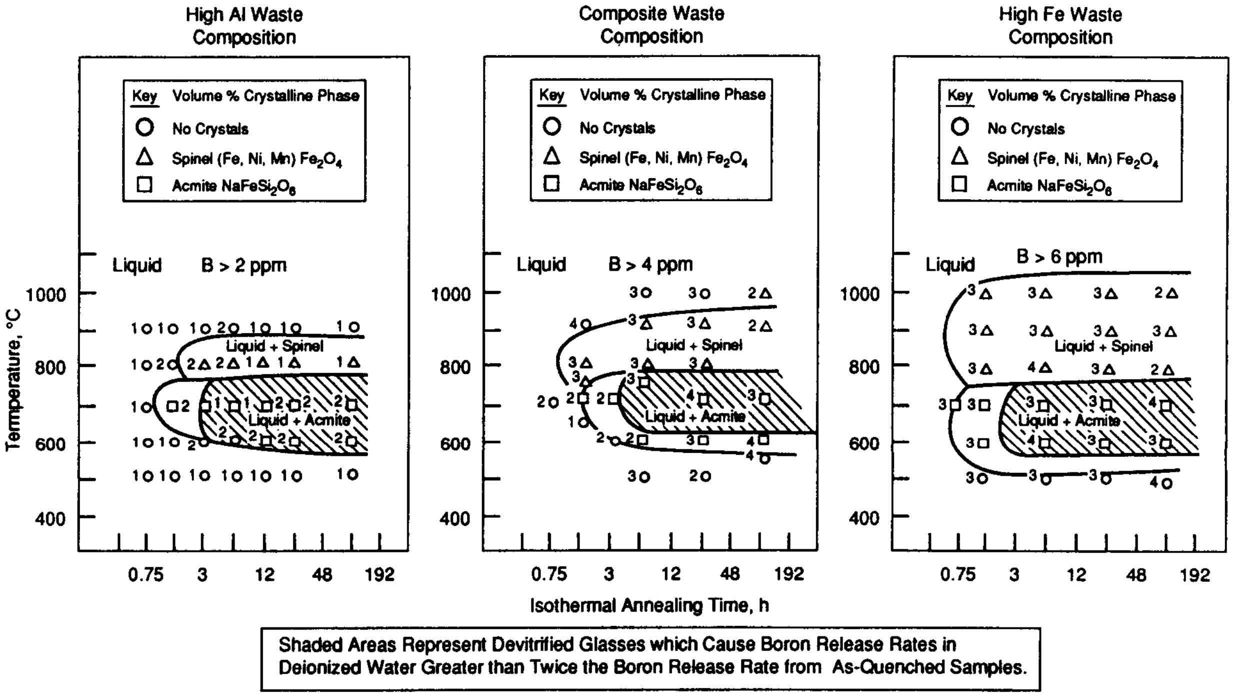


Figure 3-6. Compositions of Borosilicate Glass Showing Liquid-Liquid Phase Separation Region (I) and Homogeneous Region (II) (adapted from Schiewer, 1986)

the shaded Region I are expected to show phase separation, while compositions in the shaded Region II are expected to be homogeneous). It is important to note that partial substitution of Na_2O with Li_2O could extend the field of phase separation beyond the Region I marked in Figure 3-6 (Schiewer, 1986) towards higher SiO_2:B_2O_3 ratios, thereby making the glass more susceptible to phase separation. Therefore, in making additions of alkali compounds to glass, principally sodium and lithium, one must consider the effects of such additions on possible liquid-liquid phase separation and, as a consequence, on the chemical durability of the glass.

3.2.6 Devitrification and its Effect on Chemical Durability

Devitrification of 30 vol% in SRL 165 glass with a "composite" waste composition resulted in an increase of the corrosion rate by only a factor of three, as measured by boron release (Jantzen and Bickford, 1985). Formation of spinel in the devitrified glass reportedly had practically no effect on the durability, while the formation of acmite did. A similar investigation on a high alumina borosilicate glass, SRL 165HiAl glass, is also reported in the literature (Bickford and Jantzen, 1984). As with the glass SRL 165 "composite" waste, acmite formed in this glass upon annealing. However, very little spinel, $Ni(Fe_{0.5}Cr_{0.5})_2O_4$, formation (less than 1 vol%) was observed. Figure 3-7 (Jantzen and Bickford, 1985)



Shaded Areas Represent Devitrified Glasses which Cause Boron Release Rates in Deionized Water Greater than Twice the Boron Release Rate from As-Quenched Samples.

Figure 3-7. Time-Temperature-Transformation (TTT) Curves for Type SRL-165 Glasses of Three Different Compositions (Jantzen and Bickford, 1985) shows that boron release rates are affected little by devitrification in this glass. On the other hand, the chemical durability of SRL 165 glass with high Fe is much more affected by crystallization. This difference in the behavior of the two glasses is explained on the basis of acmite yield and cracking upon cooling of isothermally annealed samples. It is also reported that samples cooled slowly after isothermal annealing had comparable volume fractions of acmite but did not show a major deterioration of chemical durability. The results of another study on the effects of crystallization of borosilicate glass on aqueous leaching are shown in Figure 3-8 (Reimus et al., 1988). The figure shows boron release data for the isothermally heat-treated glasses plotted as a function of heat treatment time and temperature on the TTT diagram. A maximum decrease of a factor of 2 in the durability was found for the isothermally heat-treated samples after annealing treatment at 500°C for 2 hours versus 600°C for 240 hours.

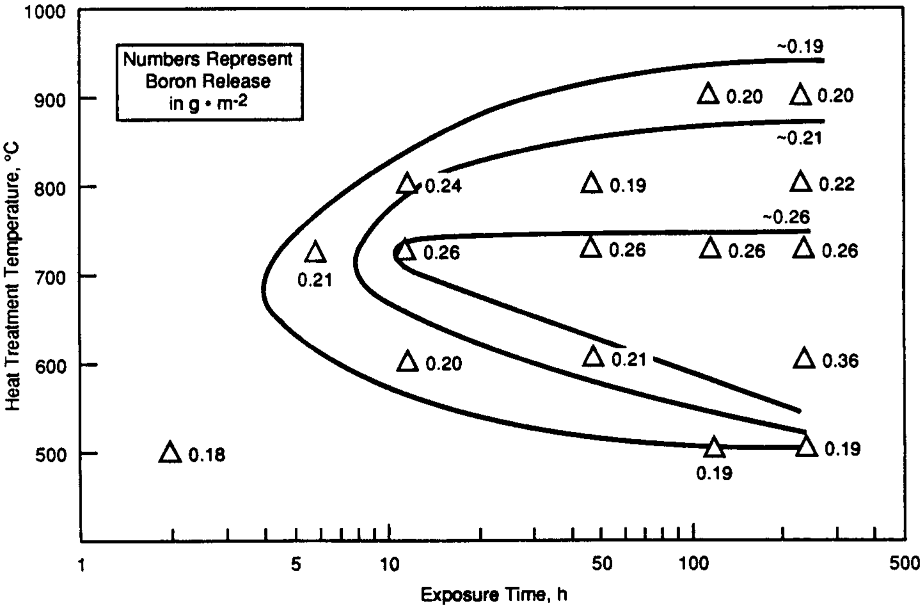


Figure 3-8. Time-Temperature-Transformation (TTT) Curves for Boron Releases for Isothermally Heat-Treated WVCM-50 Glass (Reimus et al., 1988)

3.3 MECHANICAL PROPERTIES

Glass is a brittle material; as a consequence, fracturing properties need to be considered in the evaluation of the performance of the wasteform. Fracture is inevitable in large-scale glass blocks unless cooling periods are extended from days to weeks or months. However, very slow cooling has other undesirable effects, such as devitrification of the wasteform and slower production rate. Therefore, the cooling rates are optimized to reduce cracking as well as the amount of the formation of devitrification products. The main consequence of the fracturing is to increase the glass surface area and formation of respirable fines ($\leq 10^{-5}$ m). Typical data for the mechanical properties of borosilicate waste glasses show that the Young's moduli range from 81 to 90 GPa, thermal conductivity from 6.1 to 9.1 $W \cdot m^{-1} \cdot K^{-1}$, coefficient of thermal expansion from 8.31 to 9.9 × 10^6 K^{-1}, specific heat from 0.837 to 0.88

$J \cdot g^{-1} \cdot K^{-1}$, and Vickers microhardness from 6.1 to 9.1 GPa. These values are only slightly different from those of other nonradioactive glasses (Lutze and Ewing, 1988). The temperature dependence of the fracture surface energy for an alkali borosilicate glass frit reportedly exhibits surface energy decrease with increasing temperature. A minimum value of $3.7\ J \cdot m^{-2}$ at 280°C is reported (Okafor and Martin, 1988). The value at room temperature is $5.5\ J \cdot m^{-2}$. The implication of this trend is that the fracture surface energy would be lower for the first few hundred years in the repository when the wasteform temperature is higher. As a result, greater amounts of glass fracturing could occur in the earlier years if a seismic activity were to be experienced at the repository site. The consequences of the observed temperature dependence of glass fracture energy need to be factored into radionuclide release models for the repository.

Tests performed on stainless steel canisters filled with simulated nuclear waste glass with impact energies ranging up to $630\ J \cdot kg^{-1}$ show an increase in the surface area by a factor of 40 relative to the geometric area of the glass monolith (Smith and Ross, 1975). The mass fraction of the glass of respirable size was reported to be 0.01 wt%. From the limited tests conducted, a nearly linear relationship between the impact energy and increase in the surface area could be inferred; however, no scale-up of the data to full-size canisters was possible. Evidently, such a large increase in the surface area could greatly increase the release of radionuclide upon contact of the fractured glass with water. However, the probability of such high impact energies being imposed on the wasteform during transportation or as a result of a seismic activity during storage in the repository need to be evaluated.

The thermal expansion coefficients of the glasses being considered for vitrifying radioactive wastes are generally in the range of 7 to $12 \times 10^{-6}{}^{\circ}C^{-1}$ between ambient temperature and 400°C. These values are lower than those of steels being considered for canisters in which the glass will be poured, which are typically in the 15 to $17 \times 10^{-6}{}^{\circ}C^{-1}$ range (Marples, 1988). This difference between the coefficients of thermal expansion of the glass and the metallic canister is known to lead to fracturing of the glass during cooling of the monolith. The reported increases in the glass surface area due to fracturing range from two to four times for annealed or slow-cooled canisters to 12 times for canisters cooled by free air convection. Increases for faster cooling rates (e.g., water quenching) can be as high as 20 times or more (Slate et al., 1978). Increased surface area would increase release of radionuclides upon contact of the fractured wasteform with water.

3.4 RADIATION EFFECTS

3.4.1 Sources of Radiation

The principal internal sources of radiation in HLW are α-decay of the actinides and β-decay of the fission products. The energy release per decay event is typically on the order of 1 MeV for β-decay to 5 MeV for α-decay. The main sources of α-decay are the isotopes of uranium, neptunium, plutonium, americium, and curium. Though the total β-decay is highest in a freshly discharged spent fuel, the relative number of displacements is negligible because of the small number of displacements per event. The highest number of displacements per event is associated with fission fragments, but in this case, the intensity is low. Thus, spontaneous fission contributes least to the total number of displacements in the glass. Their radiation intensity is governed by the waste loading in the glass. In general, β-decay of the fission products is expected to dominate during the first few hundred years in a period of high radioactivity and high heat generation, while α-decay will dominate at longer times. The cumulative α- and β-decay events projected for waste glasses from WVDP and DWPF are similar and are shown in

Table 3-2 (Weber, 1991) for storage times up to one million years. The cumulative absorbed radiation doses are also given in Table 3-2 (Weber, 1991). In the case of borosilicate glasses, incorporating reprocessed commercial nuclear fuel from countries other than the U.S., the cumulative decay events and absorbed doses could be a factor of 100 higher than those listed in Table 3-2 (Weber and Roberts, 1983; Burns et al., 1982).

Table 3-2. Cumulative Decay Events and Doses Projected for WVDP and SRP Nuclear Waste Glasses (Weber, 1991)

Time (years)	Alpha Decays (per gram)	Beta Decays (per gram)	Alpha Dose (rad)	Beta and Gamma Dose (rad)
1	2×10^{14}	5×10^{16}	2×10^{7}	6×10^{8}
10	2×10^{15}	5×10^{17}	2×10^{8}	6×10^{9}
10^2	2×10^{16}	2×10^{18}	2×10^{9}	3×10^{10}
10^3	1×10^{17}	5×10^{18}	9×10^{9}	6×10^{10}
10^4	3×10^{17}	5×10^{18}	3×10^{10}	8×10^{10}
10^5	5×10^{17}	5×10^{18}	4×10^{10}	1×10^{11}
10^6	1×10^{18}	5×10^{18}	8×10^{10}	1×10^{11}

3.4.2 Simulation Techniques

The radiation effects on glass wasteforms are a result of the decay of the incorporated radionuclides. The effects of radiation accumulate over the decay time of the radionuclides and thus can be considered to occur on a geologic time scale. Consequently, all laboratory experiments on radiation effects must be accelerated simulations. The long-term effects of α-decay in HLW glass are generally simulated by doping (incorporating) a short-lived actinide isotope into the glass. The commonly used short-lived α-emitters are: ^{242}Cm ($t_{1/2}$ = 163 d), ^{244}Cm ($t_{1/2}$ = 18.1 y), ^{241}Am ($t_{1/2}$ = 432.6 y), and ^{238}Pu ($t_{1/2}$ = 87.7 y). Doped samples can reach α-event doses equivalent to that expected for commercial HLW glass in 10^4 to 10^6 years in only a few years in laboratory experiments. Dose rates are typically increased by a factor of more than 1,000 for ^{244}Cm and ^{238}Pu, the two most frequently used isotopes for doping glass. The doping levels for the laboratory samples typically range from 0.5 to 5 wt%. However, higher doping concentrations of up to 8 wt% have been used. High doping levels can lead to inhomogeneous distribution of the radiation source because of limited solubilities of some of the actinide oxides in the glass (e.g., PuO_2).

3.4.3 Radiation Stability

The density of radiation damaged glasses varies with dose. In some glasses, there is no change, or the effect is too small to be detectable. The density typically varies linearly with dose in the beginning, but reaches saturation at a dose of approximately 10^{25} α-decays$\cdot$m^{-3} (Turcotte, 1981). Data for a number of glasses are shown in Figure 3-9 (Weber and Roberts, 1983). The glasses shown were doped with ^{244}Cm. The calculated doses were up to 10^{25} α-decays$\cdot$m^{-3} or 4×10^{18} α-decays$\cdot$g^{-1}, assuming an

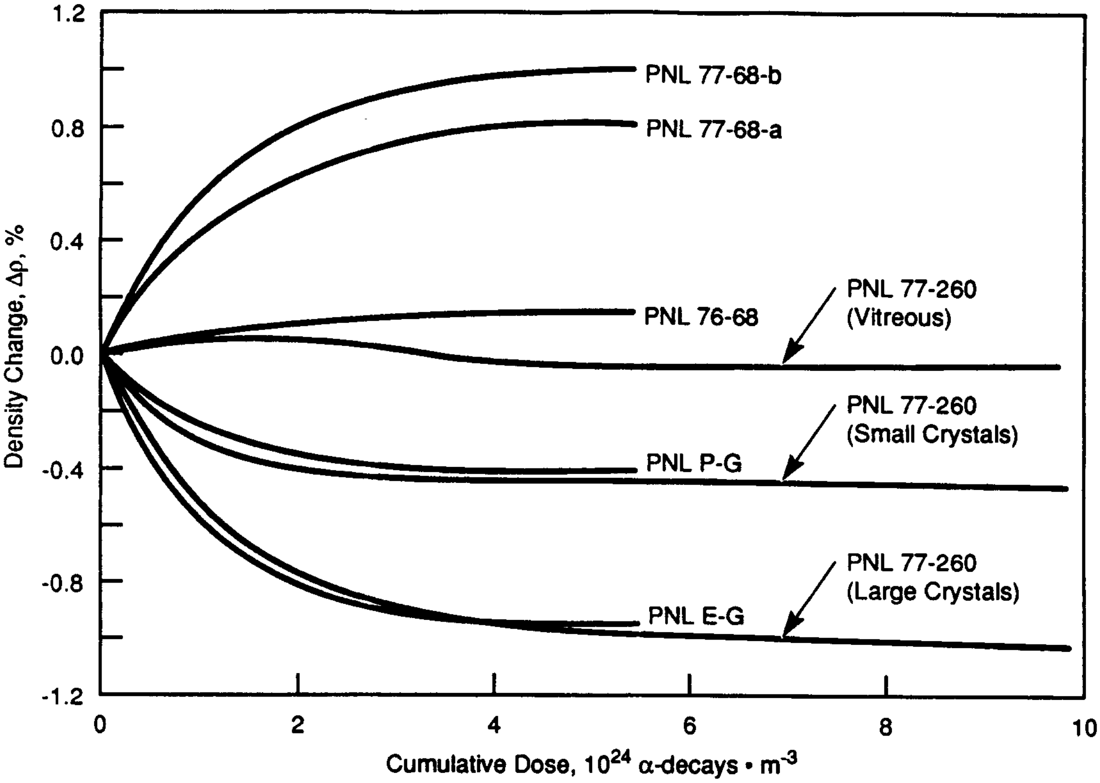


Figure 3-9. Density Changes in ^{244}Cm-Doped HLW Glasses (adapted from Weber and Roberts, 1983)

average density of 2.5 $g \cdot cm^{-3}$ for HLW borosilicate glasses. Positive and negative density changes are exhibited in the figure. There is as yet no satisfactory theory which explains why some glasses expand, while others of apparently similar composition contract when exposed to a radiation field.

The density change trends have been approximated by an exponential behavior as a function of dose according to Eq. 3-1:

$$\Delta\rho/\rho = A[1 - \exp(-BD)] \tag{3-1}$$

where ρ is the density of the glass
D is the dose (α-decays $\cdot m^{-3}$)
and A and B are material-dependent parameters (A is the density change at saturation, while B determines the rate of density change).

The values of A and B, as determined by regression analyses of the data for a number of nuclear waste glasses, are published in the literature (Weber, 1983).

The difference in density change due to α-damage between wasteforms containing defense wastes and those containing commercial wastes is shown in Figure 3-10 (Weber, 1983). From the figure, it is clear that there should be a measurable density change after just one year in a glass incorporating commercial HLW, whereas no measurable change would be expected in a defense glass wasteform for

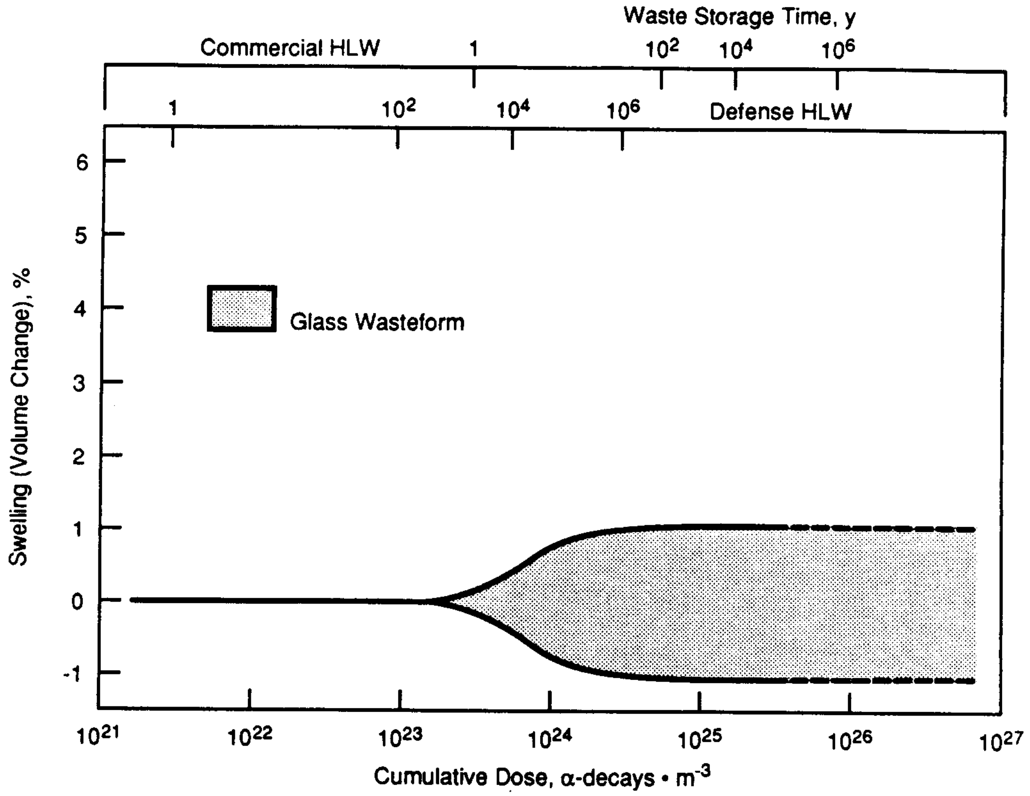


Figure 3-10. Expected Volume Changes as a Function of Dose and Storage Time for Defense and Commercial HLW Glass Wasteforms (adapted from Weber, 1983)

many years. These results indicate that specific components of the ion energy, ionization versus displacement, may be significantly different in their effectiveness in different glass structures (Arnold, 1985). It has been suggested that the B_2O_3 phase is more easily compacted than the SiO_2 phase with the implication that phase-separated glasses may be more susceptible to radiation damage than homogeneous glasses (Arnold, 1985).

3.4.4 Gamma Irradiation

There have been no literature-reported studies on glass wasteforms that measured volumetric changes in glass as a function of gamma radiation dose. However, an experimental study has investigated the density change in SiO_2 and several commercial borosilicate glasses irradiated with ^{60}Co gamma irradiation in the 10^8 to 10^{11} rad dose range (Weber and Roberts, 1983). The radiation-induced densification was observed to increase with dose and apparently with boron content of the glass. The maximum compaction observed was approximately 1.0 vol%, as illustrated in Figure 3-11 (Shelby, 1980). In another study, the effect of gamma radiation on the durability and microstructure of a simulated DWPF nuclear waste glass was investigated. Glass samples were irradiated with ^{60}Co source up to a maximum dose of 3.1×10^{10} rad. Samples were then leached at 90°C in deionized water to study the effects of radiation on the chemical durability of the glass. The results showed that gamma radiation did not affect

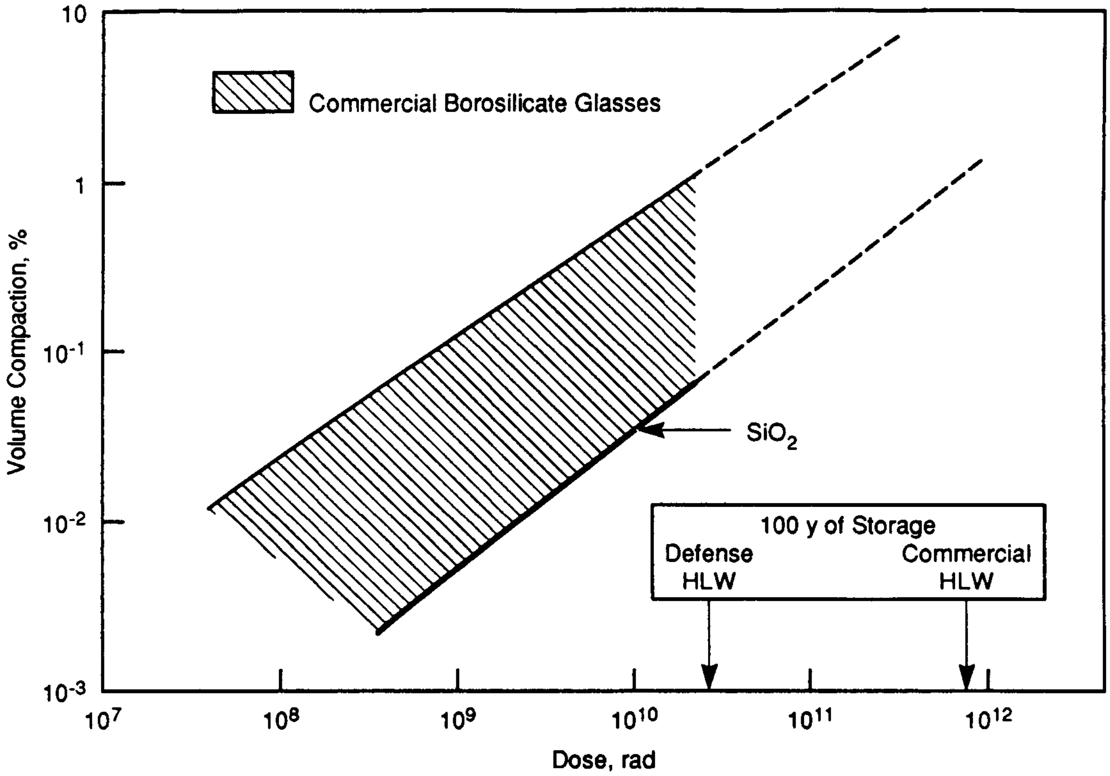


Figure 3-11. Volume Compaction in Fused Silica and Commercial Borosilicate Glasses as a Function of Radiation Dose (Shelby, 1980)

the leachability of the glass. No microstructure damage was evident either. However, severe damage reportedly could be induced by the electron beam from the microscope (Bibler et al., 1990).

3.4.5 Stored Energy

Stored energy, as a result of the decay of radionuclides, has been studied extensively to determine whether a sudden release of energy might occur and lead to a rise in the temperature of the wasteform monolith. Calorimetric methods can be used for measuring such releases. If enough energy is released, crystallization and cracking of the glass could result. As with density changes, stored energy increases with increasing radiation dose up to a limit. Saturation at approximately 10^{25} α-decays$\cdot$m^{-3} at room temperature has been reported for glass wasteforms (Weber and Roberts, 1983). Actinide doping technique has been the most frequently used to study the stored energy in glasses for HLW. The stored energies as a function of cumulative dose for a number of waste glass compositions is shown in Figure 3-12 (Roberts et al., 1981). This figure shows that the buildup of stored energy follows exponential behavior similar to the change in density. Saturation value is reached in the range of 80 to 130 J$\cdot$g^{-1}. As shown in the figure, the saturation values appear to be glass-type dependent, but it is attained in all cases at approximately 1×10^{24} α-decays$\cdot$m^{-3}. An example of the rates of stored energy release in a glass as a function of temperature and cumulative dose is shown in Figure 3-13 (Roberts et al., 1976). The energy releases for the PNL-72-68-a glass occur over a broad range of temperature, and a two-stage

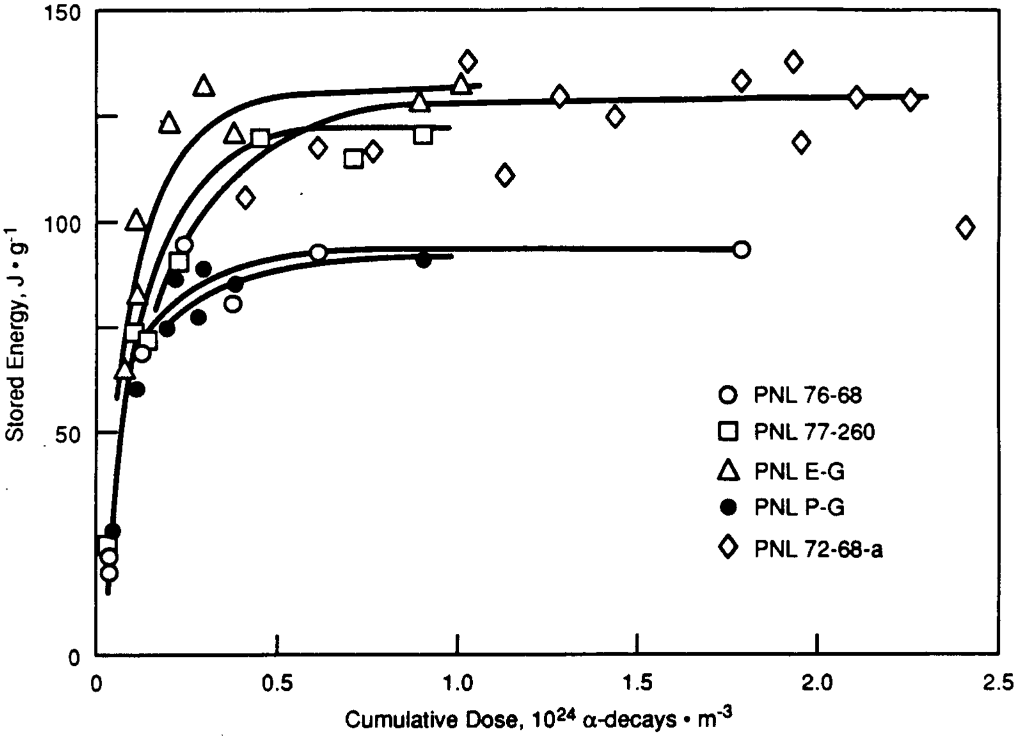


Figure 3-12. Stored Energy in ^{244}Cm-Doped HLW Glasses (Roberts et al., 1981)

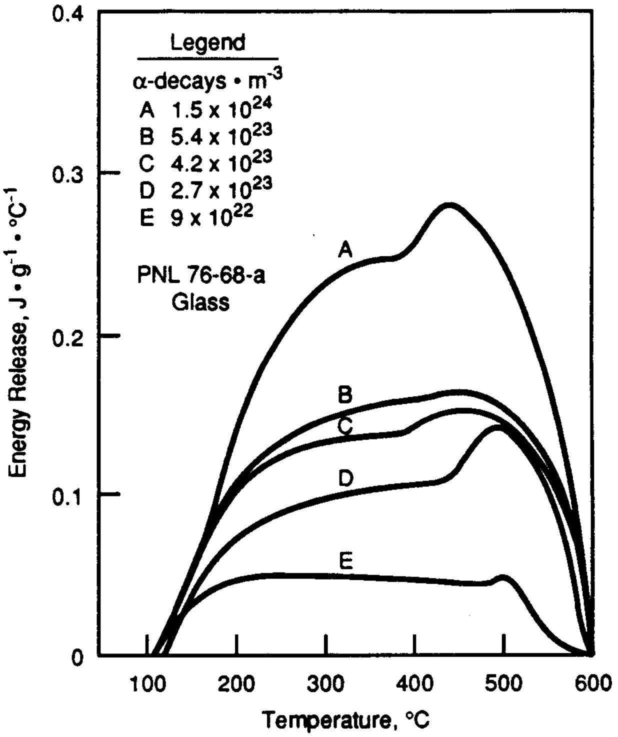


Figure 3-13. Stored-Energy Release Rates of ^{244}Cm-Doped PNL 72-68-a HLW Glass as a Function of Temperature (adapted from Roberts et al., 1976)

release mechanism has been suggested (Roberts et al., 1976). A sudden release of stored energy was not observed in this particular glass at the temperatures investigated. Figure 3-14 (Weber and Roberts, 1983) shows stored energy curves for two dose rates differing by a factor of eight. From the graphs, it can be concluded that the stored-energy release from the glass at the two dose levels investigated is independent of the dose rate.

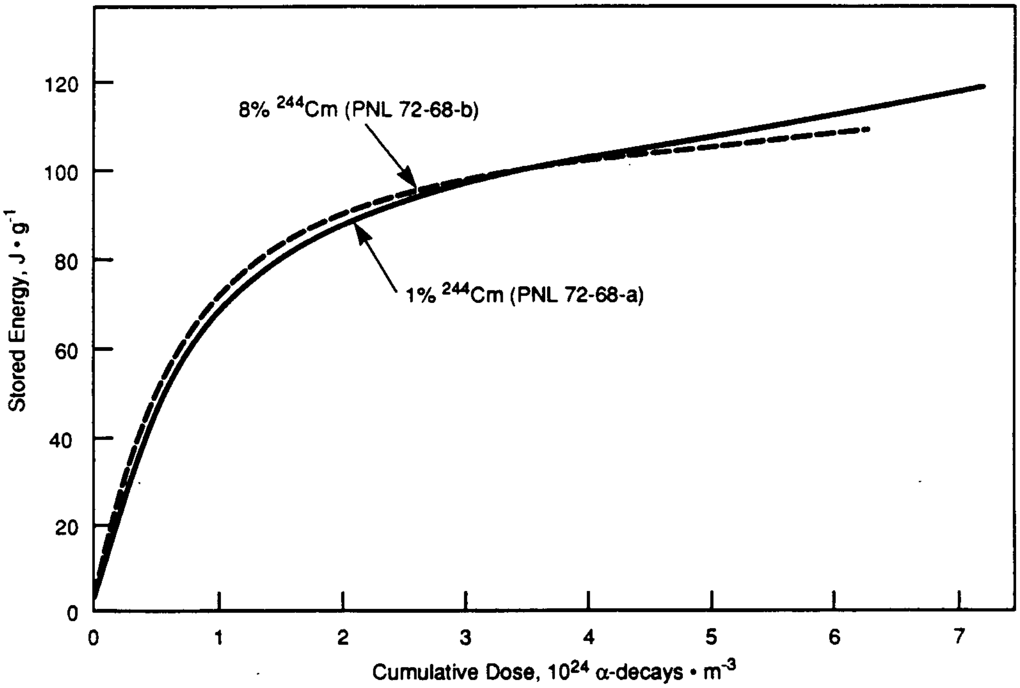


Figure 3-14. Effect of Dose Rate on Stored Energy in ^{244}Cm-Doped PNL 72-68 HLW Glass (Weber and Roberts, 1983)

3.4.6 Helium Production from Actinide Decay

A major actinide decay product that could affect the integrity of the wasteform is helium. It is important to know whether the helium atoms generated are accommodated interstitially or diffuse to internal voids or the plenum of the wasteform canister. Helium buildup in wasteform can potentially produce embrittlement, swelling from bubble formation, or pressurization of the waste canister (Malow et al., 1980; Mendel et al., 1976; Laude et al., 1976). Table 3-3 (Lutze and Ewing, 1988) lists major radioactive sources in the HLW that could lead to helium generation.

Some estimates of helium generation can be made from the data obtained from three Pu-doped simulated borosilicate waste glasses in which release of helium was measured after the samples had been stored for 2.5 years in sealed capsules at 170°C (Malow et al., 1980). During the period of storage, the glasses received a cumulative dose of 2.6×10^{24} α-decays•m^{-3}. Extrapolating the calculated diffusion coefficient values of 10^{-10} cm^2•s to 10^{-11} cm^2•s at 170°C to room temperature reportedly yielded

Table 3-3. Major Radioactive Sources and Their Decay Products in HLW Glass (Lutze and Ewing, 1988)

Time Interval (y)	Sources				Decay Products			
	1	2	3	4	1	2	3	4
$10-10^{2}$	^{137}Cs	^{90}Sr	^{242}Am	Cm	Ba	Zr	Np, He	U, He
$10^{2}-10^{4}$	^{241}Am	^{240}Pu				U, He		
$10^{4}-10^{5}$	^{239}Pu	^{243}Am	^{99}Tc			U, He	Ru	
$10^{5}-10^{6}$	^{135}Cs	^{99}Tc	^{93}Zr		Ba	Ru	Nb	
$10^{6}-10^{7}$	^{135}Cs	^{93}Zr	^{107}Pd	^{237}Np	Ba	Nb	Ag	U, He

diffusion coefficients which indicate that only a small fraction of helium can be released from the glass during such low-temperature storage. However, if the storage temperatures are higher, as in the U.S. conceptual repository design (U.S. DOE, 1988), and one of the dimensions of the monolith is small or if the fractures in the glass are taken into consideration, substantially large amounts of helium could be released into the plenum of the waste canister. Such conclusions were derived from a study involving helium diffusion in ^{244}Cm-doped PNL 72-68 glass (Turcotte, 1976). Depending on the material of construction and the design of the waste canister, most of the helium could diffuse out of the canister over several years or could lead to pressurization of the canister. High internal pressure in a metallic canister could result in an accelerated creep.

4 CHEMICAL DURABILITY AND ITS MEASUREMENT

4.1 CHEMICAL DURABILITY

Glass is one of the more chemically durable materials in common use. It is highly resistant to corrosion by water and acids, and is stable at reasonably high temperatures. Nevertheless, glass does react, albeit slowly, with various chemical environments including aqueous solutions. Since the period for calculating the performance of the HLW glass in a geological repository is very long (i.e., 10,000 years), even slow water/glass interaction phenomenon need to be understood well for developing mathematical formulations for predicting the performance. One such way is to conceptualize the degradation mode (based on reasonable hypotheses), obtain qualitative verification of the degradation phenomena and quantitative data through precise experiments under controlled test conditions, and then use the mechanistic understanding developed through the laboratory-generated information in developing predictive models. For the release of radionuclides from the glass wasteform in a geological repository, the only credible scenario is the intrusion of steam or water. Therefore, data related to water/glass interaction, both leaching and general corrosion, are considered essential to the development of performance assessment models. The term, chemical durability, as it is used for glass wasteform refers to its resistance to attack by aqueous solutions measured as a rate of dissolution (e.g., $g \cdot m^{-2} \cdot d^{-1}$) or by elemental release (e.g., ppm or $mg \cdot L^{-1}$).

4.2 A GLASS/WATER INTERACTION

There are several reviews of mechanisms of the reaction of water with glass in the literature, some dating as far back as 200 years, but a complete understanding of the process has yet to be developed (Newton, 1985). A review of the available glass leaching models is not provided in this report. However, a simple model is given to describe glass degradation phenomenon in an aqueous environment which may lead to the release of radionuclides from HLW glasses.

According to this model (Doremus, 1979), at least three different steps are involved in the reaction of water with a silicate glass containing alkali ions (such as borosilicate glasses for HLW): (i) ion exchange of hydronium (H_3O^+) or hydrogen ions from the water with alkali ions in the glass, (ii) partial hydration of the silicon-oxygen network of the glass, and (iii) dissolution of the glass into the contacting solution. Either or both of the first two steps can be absent, depending upon glass composition or solution pH, and the third is absent when the glass reacts with water vapor instead of liquid water or a solution. A schematic of the variation in the concentration of alkali ions on the surface of an alkali silicate glass after reaction with water is shown in Figure 4-1 (Doremus, 1979). The bulk glass contains alkali ions at their original concentration; however, the concentration of alkali ions steadily decreases towards the free surface of the glass as a result of their replacement with hydronium ions. In the layer of partial exchange (intermediate layer), the network structure of the glass is intact, and the only change is replacement of one ion for another. Closer to the glass free surface, the network can become partially hydrated by the reaction of silicon-oxygen bonds with water. The reaction has been described as shown in Eq. 4-1.

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}} + H_2O = -\overset{|}{\underset{|}{Si}}OH\ HO\overset{|}{\underset{|}{Si}}- \qquad (4\text{-}1)$$

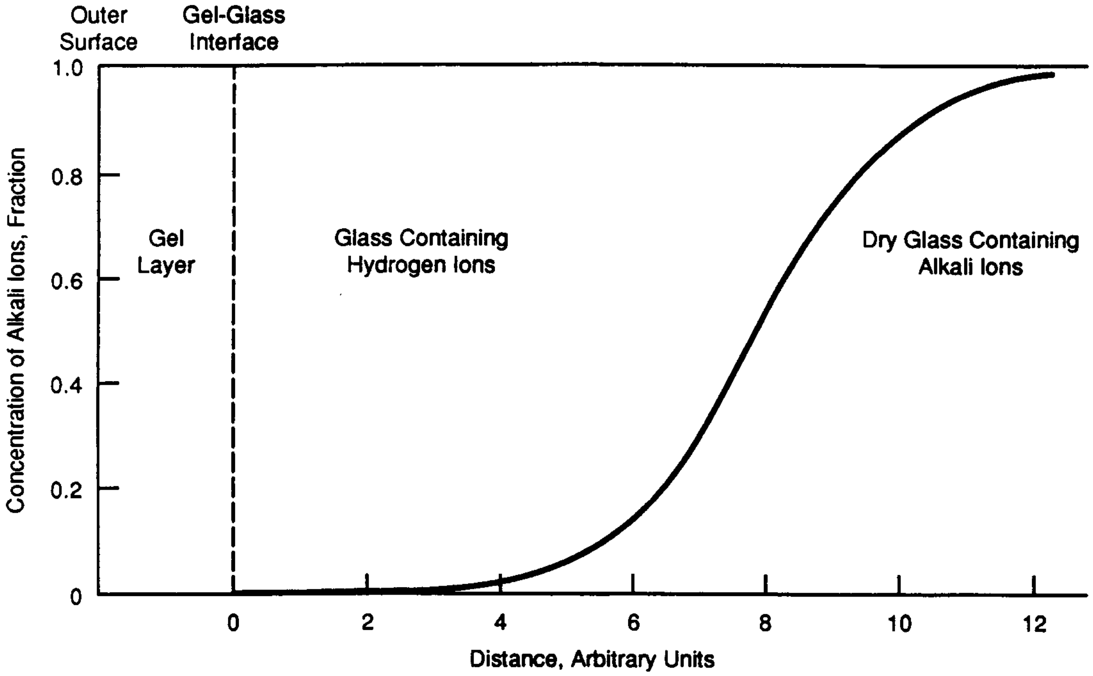


Figure 4-1. Schematic of Surface Hydrated Layers on Alkali-Silicate Glasses (adapted from Doremus, 1979)

The partial hydration of glass at and near the glass/water interface leads to a more open structure than in the bulk (solid) glass. Ionic species from the solution and water molecules can penetrate through this partially hydrated layer with much higher mobility than in the glass network that has not been altered by a reaction such as given in Eq. (4-1).

A number of parameters of the glass wasteform could influence the kinetics of Eq. (4-1) and, hence, the release of selected components from it or its general degradation rate (mass loss per unit time). Both effects are of interest in determining the durability of glass and, hence, its acceptability for disposal in a geological repository. In general, the durability measurements ought to provide information related to releases of ionic and elemental species from the wasteform as well as the alteration of the properties of glass itself as a result of contact with water. The altered conditions of the glass wasteform will determine the initial condition for further attack by repository waters. Such information, related to altered state of glass, would be crucial if the repository were to experience episodes of water intrusion/flooding followed by extended periods (years or decades) of dry environment. Estimates of long-term releases from the wasteforms under alternating wet/dry cycles could be substantially different (possibly greater) as compared to the scenario in which the glass wasteforms were exposed to a small amount of stagnant water. No literature-reported studies of such a phenomenon are available.

4.3 CHEMICAL DURABILITY TESTS

Chemical durability tests are the most frequently performed experiments for wasteform characterization. Test periods are typically on the order of days to months. Temperatures in most cases are between ambient and 100°C. Early studies on glass/water interactions often failed to define appropriate experimental conditions. Durability tests were generally aimed at comparing different glass formulations and for determining the leach rates for selected elements or the general mass loss of the monolith. There were no reference wasteforms, temperatures, flow rates or solution compositions, and almost no standard test methods. Thus, data from older experiments cannot be used in predicting the performance of glass wasteforms being developed now.

When attention became more focused on selection of geological formations for a HLW repository, the need for materials property data collected under standardized test conditions for the repository performance assessment studies, uncertainty analyses, and licensing procedures became more apparent. The earliest attempt to develop standardized chemical durability tests was begun with the establishment of the Materials Characterization Center (MCC) in 1979. Over a period of a decade, the MCC developed a series of reference test methods and materials. Such tests included a solubility test, measurements of wasteform performance under static leachate conditions, and slow- and fast-flowing leachate tests. Reference leachate compositions were recommended to account for different repository groundwaters. Sample preparation techniques, surface finish, size and shape (monolith versus powder), were specified in the test procedures. The sampling times of 7, 14, 28, 56 days, etc. were also recommended to compare data between laboratories. The chemical durability was required to be reported as normalized elemental loss value in $g \cdot m^{-2}$. Of all the chemical durability procedures developed by the MCC, the test procedure called MCC-1 has been the most widely used. This test uses a small monolith glass specimen, approximately 1 cm^3 in surface area, which is immersed in deionized water at 90°C for a period of 28 days. Additional details of MCC-1 and various other test methods developed by MCC are available in the literature (U.S. DOE, 1982).

Recently, a modified version of an MCC-developed chemical durability test on crushed glass, viz. MCC-3, has been developed. This test, called the Product Consistency Test (PCT), has been developed to meet the requirements of the Waste Acceptance Preliminary Specifications (WAPS) for HLW glass produced by DWPF. Specifications 1.3 and 1.4 of the WAPS require that the radionuclide release properties of DWPF glass be controlled during production, be assessed for devitrified glasses, and be assessed in a site specific repository environment (U.S. DOE, 1989). The procedure for the PCT was derived from existing MCC and other crushed glass leach tests and optimized at Savannah River Laboratory by additional experimentation. For the PCT, samples of crushed, washed, 100 to 200 ASTM mesh glass particles are leached in deionized water at 90°C for seven days. The volume of leachant (water) for the test is calculated as 10 mL for each 1 g of crushed glass sample. The pH of the final leachate is measured. The leachate is then filtered and acidified and the concentrations of the released elements in the leachate are measured. To assess the radionuclide release properties of the glass, the measured leachate concentrations of the elements have to be normalized for the amount of that element in the glass. An important point in understanding glass durability is to find a reliable quantitative indicator for the glass/water reaction. The concentration of boron has been used most frequently, since only minor amounts of boron are known to be involved in precipitation reactions (Lutze and Ewing, 1988; Scheetz et al., 1981). For the DWPF glasses, in addition to boron releases, releases of the other highly soluble elements, such as lithium and sodium, are measured. In addition to these alkali elements, the concentration of silicon in the leachate is also planned to be measured for DWPF glasses (Bibler and

Bates, 1990). Normalized releases for the radionuclides will then be compared to the releases from a reference glass to evaluate the consistency of the product during large-scale fabrications which are expected to commence in the next few years. Additional details of the PCT and its comparison with MCC-3 and other leaching tests are published in the literature (Bibler and Jantzen, 1989). The PCT durability measuring procedure for the HLW glasses is in the process of being accepted as the ASTM Standard Practice, and has officially replaced the MCC-1 test for measuring the durability of vitrified wasteforms in the U.S. program (U.S. DOE, 1991a).

The test results of a round robin between two independent laboratories involving two radioactive borosilicate glasses, namely, SRL 165/42 and SRL 200R, show that for major soluble elements, boron, lithium, and sodium, and the matrix element, silicon, each investigator obtained relative precision in the range of 2 to 5 percent (Bibler and Bates, 1990). This range is reportedly considered good precision for a test performed remotely with master slave manipulators in a shielded cell environment. Normalized concentrations for the nonradioactive and radioactive elements in the leachates measured at the two laboratories indicate that the radionuclides were released from the glass at a slower rate than the major soluble elements in the glass. For both laboratories, the normalized release rates for both glasses were in the general order $Li \sim B \sim Na > Si > {}^{137}Cs > {}^{125}Sb > {}^{90}Sr$. The final pH values in the tests with radioactive glass were consistent with those for nonradioactive glasses with similar compositions, indicating no significant effect of radiation for these short-duration tests.

4.4 COMPARISON OF MCC-1 WITH PCT

Both tests are conducted in static water which is sealed off from the external environment for the duration of the test. The MCC-1 test measures the response of glass monoliths at a surface area-to-volume ratio (SA/V) of 10 m^{-1}, while PCT measures the response of powdered glass at an SA/V of $\sim 2{,}000\ m^{-1}$ (U.S. DOE, 1982; Jantzen and Bibler, 1987). Both tests are usually performed at 90°C with deionized water as the leachant for short exposure periods (usually seven to 28 days). Because of the different SA/V ratios, the leachates in the PCT become concentrated at a faster rate than in the MCC-1 test as the glass reacts. There is an indication that differences in the resulting solution chemistries affect both the mechanism and the rate of glass reaction. It is, therefore, necessary to understand changes in the reaction which occur as the SA/V changes in order to relate glass durabilities measured in tests at high or low SA/V ratio, viz., using PCT or MCC-1 glass leaching procedure.

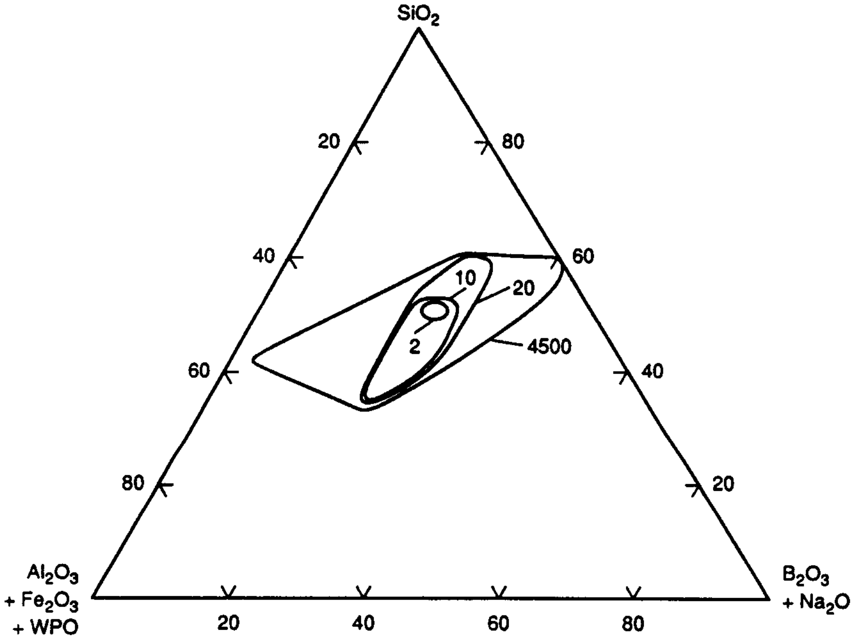
To assess the effects of the SA/V ratio on the mechanism and rate of the glass reaction, leaching tests have been performed at SA/V ratios of 10, 2,000, and 20,000 m^{-1} using actinide-doped borosilicate waste glass (Ebert and Bates, 1992). The leachate analyses show dependence of SA/V ratio of the test as the system progresses from being dominated by ion exchange to being dominated by hydrolysis and matrix dissolution as the pH increases, and finally to a system dominated by the generation of colloids. For example, the MCC-1 test predominantly measures the ion-exchange dominated reaction of the glass, while the pH remains near neutral (< 10). The PCT attains higher leachate pH values and measures the matrix-dissolution dominated rate prior to colloid or surface secondary crystalline phase formation. It is reported that observations in tests at very high SA/V ratios, such as those performed at 20,000 m^{-1}, may be dominated by secondary phase formation. Since the interpretation of glass durability using different leaching test procedures requires an understanding of which process dominates the observed response, reaction models used for long-term simulation of glass degradation must be based on experiments which probe the appropriate step in the reaction mechanism.

5 DEGRADATION OF WASTEFORM IN AQUEOUS ENVIRONMENT

The following variables have specific effects on glass and must be considered in evaluating the performance of HLW glass in aqueous environments: (i) glass composition, (ii) chemical composition and ionic strength of the leachate, (iii) pH of the leachate, (iv) redox potential, (v) flow rate, (vi) temperature, (vii) waste package components, (viii) surface layers, solubility limits, and precipitation kinetics (primarily of phases which control the concentration of silicic acid in the leachate), (ix) devitrification of the glass, and (x) radiolysis of vapor and aqueous phases. The influence of these variables on the performance/response of borosilicate HLW glasses will be discussed in this chapter.

5.1 WASTEFORM COMPOSITION

The relationship between chemical durability and the composition of nuclear waste glasses has been represented in the literature in a pseudo ternary diagram, SiO_2-($Na_2O+B_2O_3$)-other oxides, with domains of decreasing durabilities (increased leachability) based on silicon release rates in a 28-day test in deionized water at 90°C (Hench et al., 1984; Wicks et al., 1982). One such composition diagram is shown in Figure 5-1 (Hench and Hench, 1983), which plots the leachability domains as measured by the mass loss of the glass monolith in $g \cdot m^{-2} \cdot d^{-1}$ in a 28-day MCC-1 leaching test in deionized water at



Compositions in wt% for Glasses with Leach Rates of 4500, 20, 10, and 2 $\mu g \cdot cm^{-2} \cdot d^{-1}$ for SiO_2 in 28-d at a Temperature of 90°C. WPO = Simulated Waste Product Oxides Containing all Others Elements.

Figure 5-1. Domains of Constant SiO_2 Leach Rates in a 28-Day Test at 90°C in Deionized Water (adapted from Hench and Hench, 1983)

90°C. However, the potential of such an empirical approach to explain durability of glass is limited due to several exceptions that do not fit the trends on the basis of glass samples of only a few compositions.

Investigations have shown that chemically more durable glasses can be formed by optimizing certain constituents of the glass. The improved glasses generally have higher SiO_2, Al_2O_3 and Fe_2O_3 content, and are lower in alkalies (Chick and Buckwalter, 1980). The SiO_2 content in more durable glasses is typically about 60 wt%. Formation temperatures for such glasses are much higher, ranging up to 1350°C. One of the optimized formulations reportedly had a corrosion rate as low as 1/30 that of a widely studied borosilicate glass PNL 76-68 (Chick and Turcotte, 1983). Figure 5-2 (Marples, 1988) illustrates the effect of silica content on chemical durability of glass in a 30-day leaching test at 100°C in deionized water. The figure shows that in glasses with the general formula Na_2O: B_2O_3: xSi_2O, the glass corrosion rate decreases sharply as x increases from 2 to 5, and then remains reasonably constant at a rate governed by the solubility of amorphous silica in water. Another significant observation reported in the literature is that, for glass of a particular concentration of Si_2O, the aqueous leach rate is minimum when the molecular contents of B_2O_3 and Na_2O about are equal (Harvey and Jansen, 1982). The greatest advantage in the durability of the glasses of improved composition has been observed at high flow rates, which may be unrepresentative of conditions expected in an unsaturated geological repository.

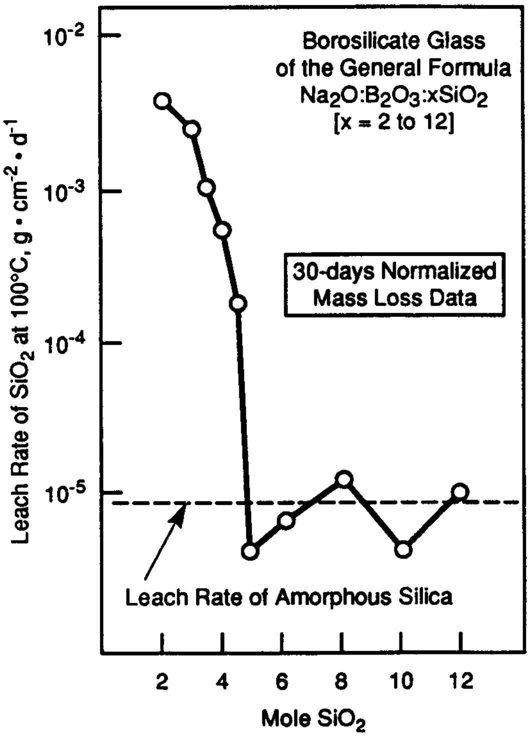


Figure 5-2. Typical Leaching Rates (Mass Loss) of Silica as a Function of Silica Content of Glass (Marples, 1988)

In another attempt to explain variations in chemical durability with glass composition, the concept of Gibbs free energy of hydration, ΔG_h, as a measure of stability has been used (Jantzen and Plodinec, 1984). Via the use of such an approach, a plot of logarithmic variation of the normalized mass loss (based on Si) with ΔG_h has been developed as shown in Figure 5-3 (Plodinec et al., 1984a). The

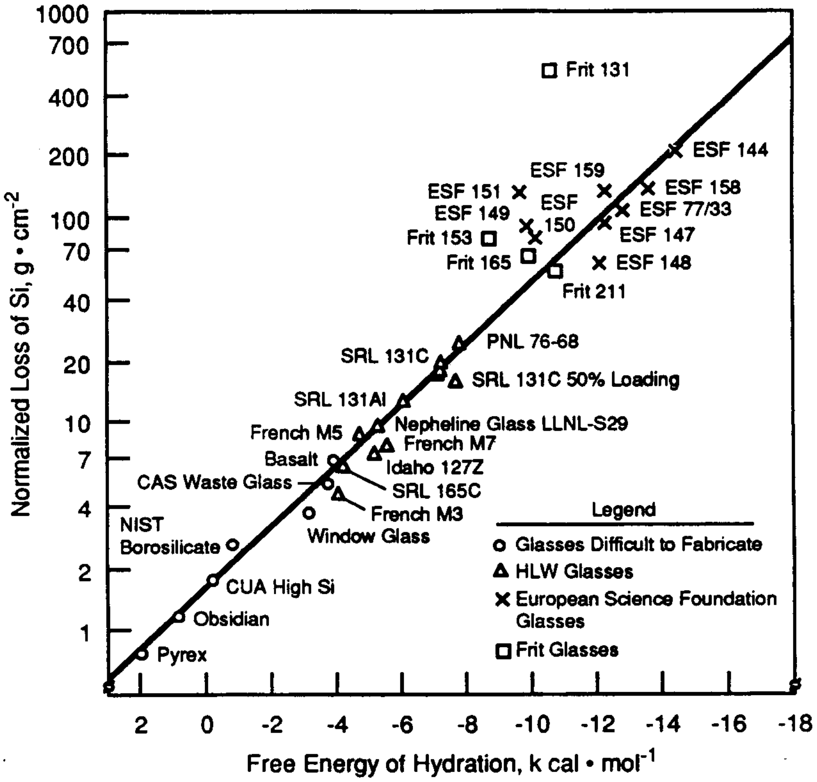


Figure 5-3. Release of Structural Silicon as a Function of Glass Hydration Energy (Jantzen and Plodinec, 1984)

basis of such a thermodynamic approach to glass degradation is to treat the glass as a solid solution of simple oxides and metasilicates and to calculate the energy difference relative to a mixture of hydrated species (hydrolysis products) in solution (Pederson et al., 1983; Plodinec et al., 1984b). An exact calculation of ΔG_h requires a knowledge of the correct speciation in solution, the structural units in the glass phase, and the respective thermodynamic data. All such essential information is currently far from being complete for borosilicate glass wasteforms. However, the results using such a simple approach can provide some understanding of glass degradation phenomena.

5.2 LEACHATE COMPOSITION

Most of the chemical durability tests have been performed in deionized water, whereas it is more realistic to use water compositions that may contact the wasteform after disposal in a geological repository. Naturally occurring waters could be dilute in ionic concentration (10^{-3} to 10^{-2} molar) or concentrated (nearly saturated salt solutions). Low ionic strength, silica bearing, neutral to slightly alkaline waters are typical of granite, basaltic, and tuffaceous rock formations, whereas highly saline, sodium- and magnesium-bearing, neutral to slightly acid solutions (brines) may be encountered in salt formations. Major ions present in natural waters include Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, HCO_3^-, and CO_3^{2-}, with many other species present at the low ppm levels. Ions introduced by the corrosion of waste package components are likely to lead to concentrations higher than those which occur naturally in the groundwaters and may have beneficial or detrimental influence on the borosilicate glass subjected to an aqueous environment.

An example of the effect of silica concentration in the water on the leaching rate of the glass monolith is shown in Figure 5-4 (Pederson et al., 1983) for the PNL 76-68 glass in a test conducted at 90°C for 28 days. The results show that the higher the concentration of silica in solution, the lower the rate of glass degradation as measured by the release of boron. The figure shows that approximately 100 ppm silica concentration in the leachate almost (but not entirely) suppresses the leaching reaction. However, even at 150 ppm silicon, a finite, albeit very small, corrosion rate is detectable. Reductions of an order of magnitude in the leach rates of some borosilicate glasses have been reported in strongly saline solutions (e.g., NaCl content of 250 g•L^{-1}) compared to those in distilled water.

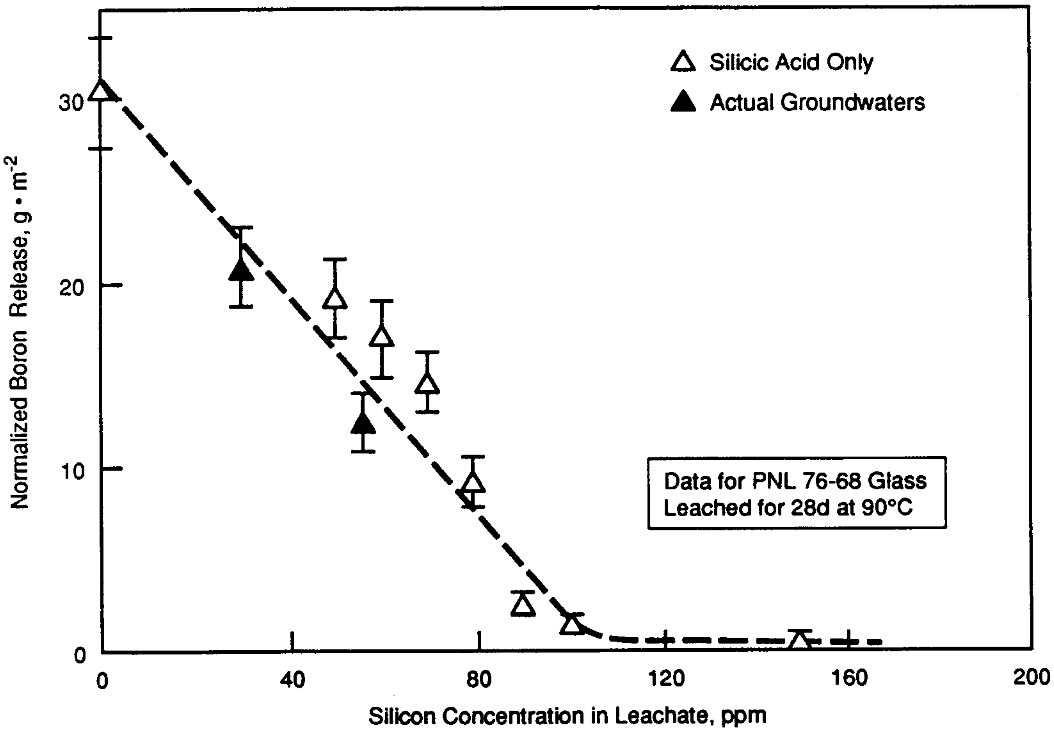


Figure 5-4. Boron Release as a Function of Silicon Content of the Leachant (adapted from Peterson et al., 1983)

The above example indicates that, if the groundwater initially contains a significant concentration of one or more of the major components of the glass (e.g., silicon), it is likely to lead to a reduced rate of reaction after a finite time. However, it has also been observed that if the leachate contains a phase that can preferentially remove one of the major glass components from solution, then the rate of glass dissolution will increase. An example of such a phenomenon is the observed increase in the leach rate of glass in the presence of iron in the leachant (McVay and Buckwalter, 1981). The observed increase in the rate of mass loss of glass has been explained on the basis of the formation of iron silicate in the leachate which leads to the reduction in the concentration of silica in solution, thereby providing a chemical gradient for additional silica in the glass to be released into the solution. Similar qualitative effect on the glass corrosion rate is reported when iron corrosion products instead of iron addition to the leachant was made. However, the explanation of the effect is different, namely, there is an indication that a sorption mechanism of silica on the iron corrosion products may be responsible for the constant removal of silica from solution until the sorption capacity is reached (Grambow et al., 1987). Independent verification of this postulated phenomenon is not available.

Results of yet another study on a related subject indicated that borosilicate glass exhibited a decrease of silica concentration after 100 days exposure in a solution which contained Mg^{2+} (Strachan, 1982). The explanation given for this observation was that silica was consumed by the formation of a solid reaction product sepiolite, $Mg_2Si_3O_6(OH)_2$. The reaction products formed only because of the presence of magnesium in the leachant. There was no magnesium in the glass. The corrosion depth on a glass monolith became constant after 200 days in distilled water, but continued to increase in brine in an identical experiment. In other corrosion experiments with concentrated salt brines, a reaction product, analcime, $NaAlSi_2O_6.H_2O$, was formed as a result of interaction of sodium, a major solution species, with the elemental releases from the glass (Lutze et al., 1983; Haaker et al., 1985).

5.2.1 Influence of Waste Package Components and Backfill Material

As mentioned earlier, release of corrosion products from the waste package could have a significant effect on the degradation of borosilicate glass. The solubility of the corrosion products and compounds of some of the likely container materials or coatings such as zinc, aluminum, iron, titanium, lead, and magnesium depend on the pH of the aqueous solution. The combination of pH-dependent precipitation, ion exchange, and glass matrix dissolution could lead to the formation of very complex surface films on the wasteform. The appearance and the sequence of precipitating phases is likely to depend on initial pH of the leachate and its changes during the experiment. The surface layer formed may be multiple in nature with various elements partitioned in selected layer(s). Such layer(s) may or may not provide protection against long-term degradation of the glass. Some examples are provided below.

Experimental evidence is available related to a decrease in the rate of PNL 76-68 glass dissolution by more than two orders of magnitude in the presence of a lead (Buckwalter and Pederson, 1982). The decrease in the dissolution rate has been attributed to chemisorption and the formation of lead silicate surface layer. A similar beneficial influence of lead on the chemical durability of SRL TDS 131 glass has also been reported (Wicks et al., 1982). However, the quantitative benefits appeared to be related to the glass type. The experimenters have attributed the significant difference between the behavior of PNL 76-68 and SRL 131 glasses to the characteristics of the lead-rich surface layers that form on the two glasses. The surface layer on PNL 76-68 was dense and stable, while that on SRL 131 was thin, nonprotective, and depleted in silica (Barkatt et al., 1984). On the other hand, a dramatic detrimental effect of the presence of iron in the leachant on the glass/water interaction is shown in Fig. 5-5 (McVay and Buckwalter, 1981). This figure shows that the presence of iron in the leachate enhances the glass corrosion rate and overrides the wide differences in the chemical composition of the three leachates used in the investigation. A qualitatively similar affect has also been reported for aluminum, namely to decrease the rate of glass dissolution. Other elements such as copper, tin, and titanium have a minor effect on aqueous corrosion of glass (Buckwalter and Pederson, 1982).

The effect of backfill material, such as bentonite, on glass corrosion rates has also been investigated. In one such study, it is reported that low ratios of bentonite/water have a detrimental effect on the glass corrosion rate (Grambow, 1987). This observation has been explained on the basis of a rise

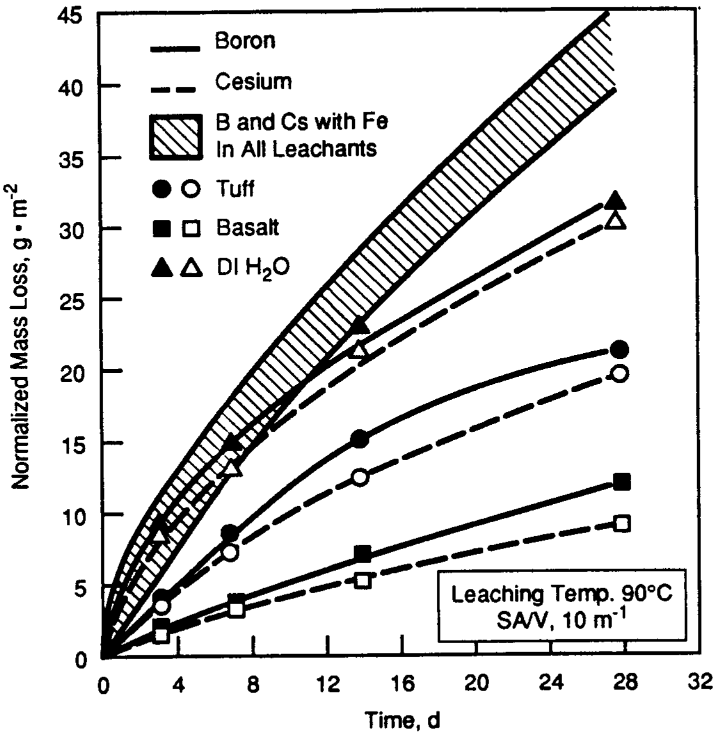


Figure 5-5. Illustration of the Effect of Iron in the Leachant on Corrosion of PNL-76-68 Borosilicate Glass (McVay and Buckwalter, 1981)

in pH, which increases the dissociation of silicic acid, and thus, delays the saturation of the leachate with respect to silica. With increasing ratios of bentonite/water, the pH shift decreases and the detrimental effect of bentonite on the corrosion rate is mitigated. Thus, high bentonite/water ratios enhance glass stability. When bentonite and iron corrosion products are present, the detrimental effect of iron prevails (Grambow, 1987). Limited literature studies are only able to provide indications of such trends. Obviously, detailed investigations on all waste package component materials are necessary to quantify the effects for optimizing the waste package materials selection and design. Currently, the U.S. waste package design does not use any backfill material. However, the material(s) selection has also not been finalized as yet, and several materials, both metallic and nonmetallic, are being considered for the various components of the waste package (U.S. DOE, 1991b; Harrison-Giesler et al., 1991)

5.3 EFFECT OF LEACHATE pH

The results of an investigation of the dependence of glass corrosion on pH, in the range 1 to 13 conducted at 25°C for 72 hours, indicates that borosilicate glass mass loss is relatively independent of the pH in the 4 to 10 range (Ross et al., 1978). A plot of borosilicate glass mass loss as a function of leachate pH from a study is shown in Figure 5-6 (McElroy and Hanson, 1986). In this figure, approximate pH ranges of a number of repository groundwaters are indicated for comparison. It is

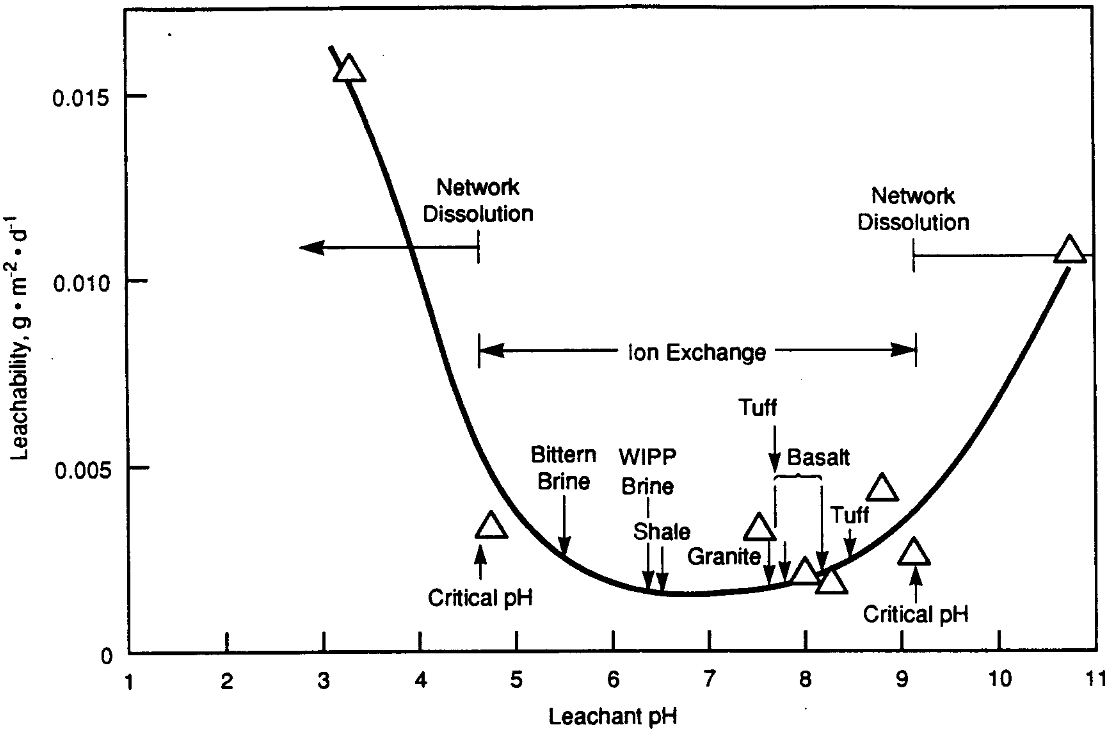


Figure 5-6. Mass Loss of Borosilicate Glass as a Function of Leachant pH (McElroy and Hanson, 1986)

apparent that borosilicate glasses become fairly unstable in stronger acid and alkaline solutions (i.e., outside of the pH 4 to 10 range).

Depending on the experimental conditions, the pH could be constant (buffered solution) or could change as a function of mass loss of the sample. For example, in a closed system with a large sample SA/V ratio, the species released from the glass, mostly alkalies in short-term experiments, will eventually accumulate in the leachate and will change the pH to higher values, typically in the 8.5 to 10 range in deionized waters. The pH values reported for SRL TDS-131 glass were up to 10.8 after 90 days, but stabilized at values above 9 after two years in a 3.5-year leaching test (Wicks et al., 1986).

In another set of investigations involving leaching of SRL TDS-131 glass over two years at 40°C and 90°C, pH values were constant at 7.8 for the experiments at 40°C up to one year test exposure and dropped to 7.2 thereafter. While in the 90°C experiment, pH values stabilized at 8 after one year in the salt solution, and at about two pH units higher in other leachants (Strachan et al., 1985; Jones, 1982). As expected, the glass corrosion rates were lower in the brines than in dilute solutions. Even higher leachate pH values of up to 12 have been reported after exposures of borosilicate glasses to static water at 90°C using high SA/V ratio test conditions (Harker and Flintoff, 1987). Such high solution pH values are attributed to alkali release from glass in confined systems leading to an increase in glass dissolution rates by up to an order of magnitude. However, different glass components can exhibit quite different pH dependence. For example, for network formers and intermediates capable of forming insoluble products in solution, leach rates can increase by several orders of magnitude at high pH. Variations in pH with time for dilute solutions have been related to the formation of surface reaction products, but the effects in high ionic strength solutions are difficult to interpret (Strachan et al., 1985).

5.4 REDOX POTENTIAL

Several fission product and actinide elements can occur in various valence states and are, therefore, susceptible to redox reactions depending on the electrochemical potential of the wasteform environment. The reactions of long-lived radioelements, such as technetium and several other actinides, after their release from the glass matrix, are of particular interest, because their solubility in aqueous solutions depends on their oxidation state. For example, U^{+6} is soluble, while U^{+4} is insoluble; and Tc^{7+} is soluble, but Tc^{4+} is nearly insoluble (Freeborn and White, 1984). Under repository environmental conditions, such elements would either dissolve or form a solid alteration product surface layer on the glass. The long-term leaching behavior of the glass wasteforms, as a consequence, will be a function of the oxidation states of such radionuclides.

The corrosion of the glass matrix is not expected to be significantly affected by the oxidation potential of the leachant, because silicon, boron, and aluminum, the principal network formers in many borosilicate HLW glasses, do not undergo valence changes within the expected Eh range in a geological respository. However, the corrosion of some borosilicate glasses high in iron concentration, such as SRL 165 (which contain 9.2 wt% Fe_2O_3), could be influenced by the Fe^{2+}/Fe^{3+} ratio. In a leaching study on SRL 165 glass, lithium and boron analyses indicated a factor of two increase in the leachability under anoxic relative to oxic conditions. Other redox active elements are also reported to be at lower concentrations in the leachate under anoxic than under oxic condition (Jantzen and Bibler, 1986). However, SRL 165 glass did not undergo any significant corrosion in the absence of oxygen in a 28-day leaching test at 90°C when in contact with a silica saturated solution and crushed basalt (Jantzen and Wicks, 1985).

In another experimental investigation, the chemical durability of the WVDP borosilicate glasses was not significantly affected by the variation of glass redox state over the Fe^{2+}/Fe^{3+} ratio range of 0.07 to 0.42 (Reimus et al., 1988). However the pH of the leachate was observed to increase with increasing Fe^{2+}/Fe^{3+} ratio. This increase was attributed to Fe^{2+} oxidation in the leachate and was explained on the basis that, as Fe^{2+} goes into solution, it is oxidized by dissolved O_2 in the following reaction:

$$O_2 + 4H^+ + 4Fe^{2+} \rightarrow 4Fe^{3+} + 2H_2O \qquad (5\text{-}1)$$

This reaction consumes H^+, which in turn increases the pH. With greater Fe^{2+}/Fe^{3+} ratios, more Fe^{2+} is available for oxidation. The greater the amount of Fe^{2+} oxidized, the greater the increase in solution pH. Calculations comparing available Fe^{2+} concentrations and H^+ consumption support this theory (Reimus et al., 1988).

5.5 EFFECT OF TEMPERATURE

The influence of temperature on glass corrosion is probably the least understood, but one of the most critical parameters in the evaluation of the long-term performance of the borosilicate glass. Since the reaction rates are low at low temperatures (e.g., below 50°C), the corrosion experiments must be run over years to obtain experimental data. This is not practical. The process can be accelerated appreciably at higher temperatures (e.g., above 100°C), leading to measurable degradation of glass within days or weeks. At even high temperatures, above 250°C, very rapid alteration of borosilicate glasses can occur in water (McCarthy et al., 1978). However, the crystalline phases produced at the surface may be different from those that form at lower temperatures. As a consequence, preferential sequestering of radionuclides in the crystalline phases may also be different. Therefore, the extrapolation of higher temperature glass corrosion data require detailed understanding of the corrosion mechanism, such as sequence of alteration layers and crystalline product formation, stability of metastable phases, and other phenomenological details, such as pH, flow rates, silica concentration in solution, etc. In the absence of a mechanistic understanding of the effects of temperature on the wasteform degradation phenomena, the information derived from high-temperature experiments may not allow one to predict the performance of glass at lower temperature with any degree of certainty.

The results of a study on the effects of temperature on leaching of borosilicate glass are summarized in Figure 5-7 (Vernaz et al., 1988). The figure shows that normalized silicon and boron mass loss against inverse of absolute temperature, 1/T, followed an Arrhenius law up to approximately 250°C with relatively little dependence on the exposure time. The average activation energy for silicon and boron is calculated to be ~ 30 kJ$\cdot$mole^{-1} between 100°C and 250°C. However, when the temperature exceeded 250°C, the activation energy increased to about 150 kJ$\cdot$mole^{-1}, indicating a possible change in the glass degradation mechanism or in some of the rate determining steps.

Analysis of the leached specimens indicated a surface layer thickness increase from 1.5 to 30 μm in 28 days with the test temperature increase from 100°C to 250°C (Vernaz et al., 1988). The surface alteration of the glass was of the same nature (i.e., a layer enriched in zirconium and rare earths next to the pristine glass), with a fine foliated texture enriched in iron and zinc on the outer (free) surface. However, alteration of the wasteform increased sharply between approximately 250°C and 300°C, with an observed surface layer thickness increase from 30 μm to 3 mm for the same 28-day test duration. Optical microscopy of the test samples, from this higher temperature exposure, revealed at least seven different sublayers (Vernaz et al., 1988). In addition, the leachate analyses showed that the effect of temperature was not the same on the rate of release of various elements. For example, comparison of leaching tests at approximately 100°C with those at 250°C show that: (i) boron, sodium, lithium, and molybdenum concentrations in solution increased by a factor of 27 to 43 at the higher temperature; (ii) glass mass loss was 22 times higher; and (iii) aluminum, calcium, strontium, zinc, iron, and zirconium concentrations were only slightly affected. Analyses of leachate from higher temperature tests, conducted between approximately 250°C and 300°C, showed concentration increase of various elements from 10 to 20 times only (Vernaz et al., 1988). Thus, the solution analyses also indicate a possible change in the glass alteration mechanism with increase in temperature.

From the above discussion, it is apparent that the influence of temperature may not be simple, and that extrapolation of high temperature data to the lower temperature of geological repository interest may not be valid due to the change in the glass degradation mechanism and/or reaction path. The threshold of approximately 250°C for the change in degradation mechanism suggested here may not be

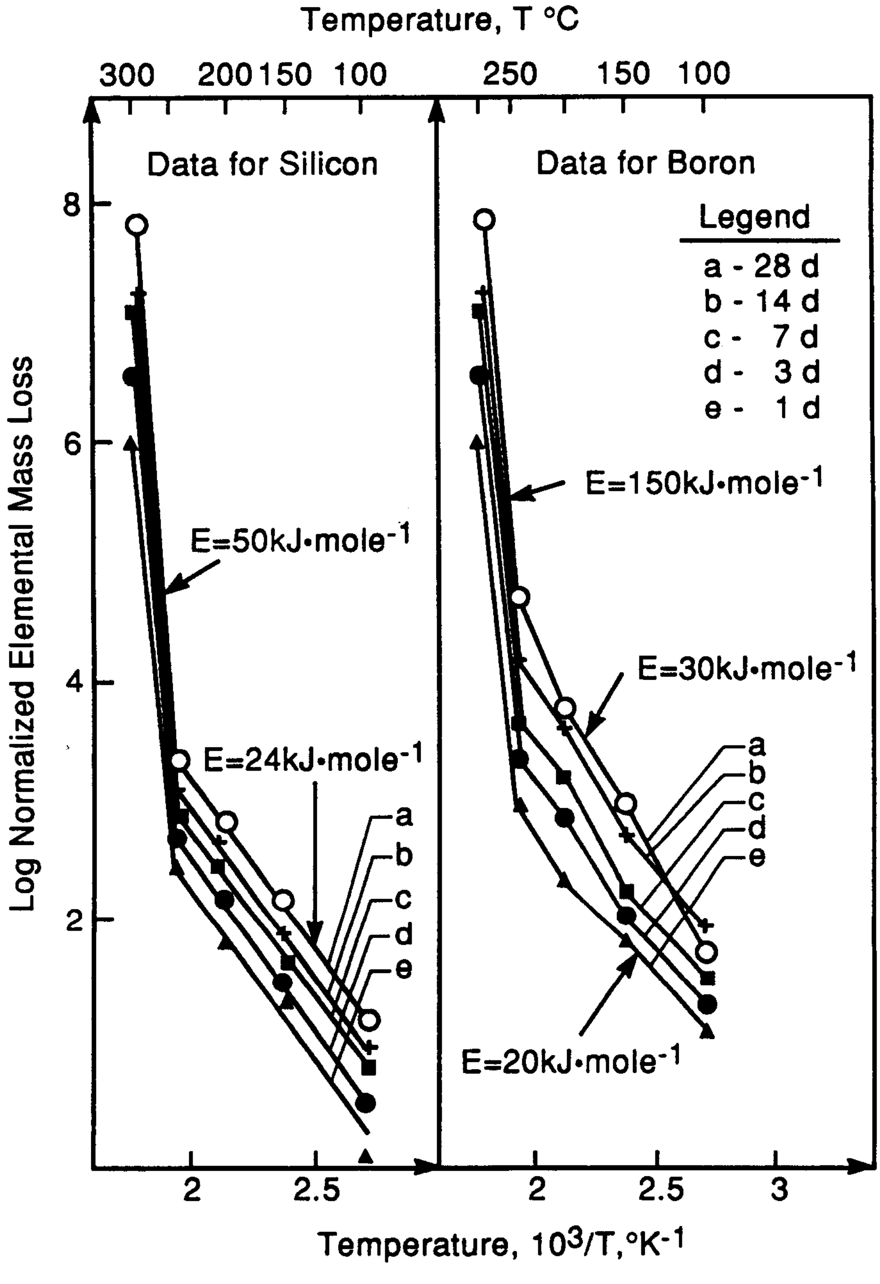


Figure 5-7. Normalized Elemental Mass Loss Versus Temperature for Different Leaching Durations (Vernaz et al., 1988)

applicable to all borosilicate glasses and may be sensitive to other properties of the wasteform or the environment. Therefore, the results obtained from the laboratory process of accelerating the glass corrosion rate via increase in the testing temperature require careful interpretation.

5.6 FLOW RATE OF THE LEACHATE

5.6.1 Static Leachate

Although it is known that groundwaters in geological repositories have a finite, albeit small, flow rate, most of the leaching tests continue to be conducted under static leachant conditions, such as specified in MCC-1 test (U.S. DOE, 1982). In such tests, the observed rate of approach to saturation is increased as the specimen surface to leachant volume ratio increases. Other significant observations of such fixed-volume static water tests are that the use of silica-enriched water decreases the short-term rate of glass corrosion, while waste-package components, such as iron, enhance the leaching rate.

5.6.2 Flowing Leachate

The dependence of glass corrosion rate, as measured by mass loss, on flow rate is shown schematically in Figure 5-8 (Marples, 1988). The graphical representation exhibits a corrosion rate limited

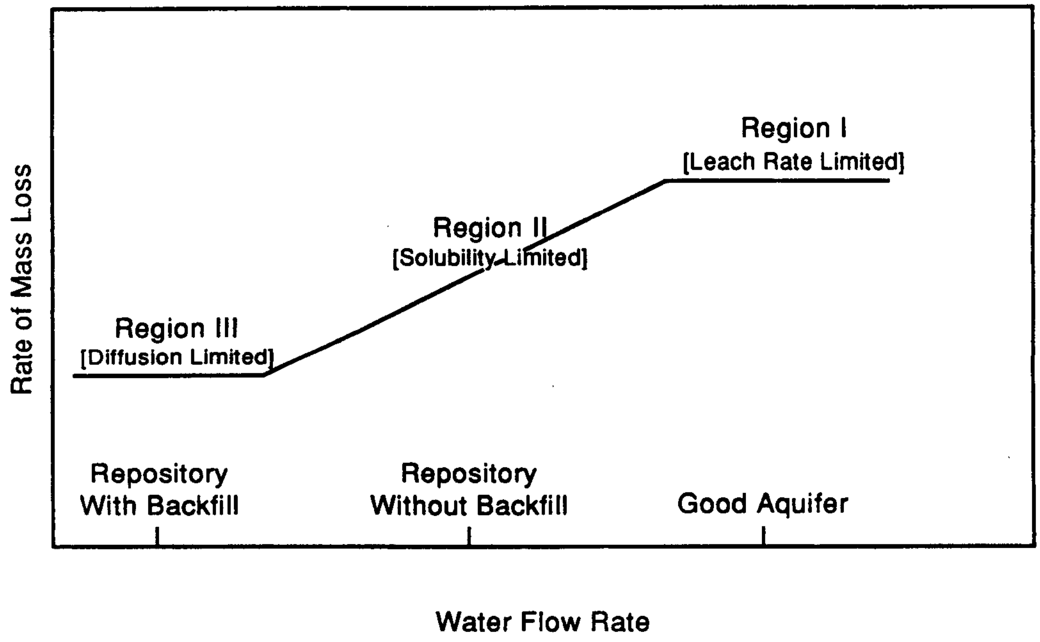


Figure 5-8. Schematic of Mass Loss as a Function of Leachant Flow Rate (Marples, 1988)

portion of the curve at high flow rates, a water access limited portion at intermediate flow rate, and a diffusion limited portion at a low to very low flow rate. There is substantial literature on glass corrosion at 90°C in deionized water which lends support to the general pattern shown in Figure 5-8 (Marples, 1988). However, the low flow rate independent part of the curve is still not well understood. The degradation of HLW borosilicate glasses show similar trends, namely, mass loss is proportional to the flow rate if the flow rate is not too high or too low. The leach rate dependency decrease as the flow rate increases is shown, for the release of silicon and sodium, in Figure 5-9 (Hench et al., 1986) for the SRL 131 glass. In this figure, only two regions of leaching behavior are shown. In Region 1, the leach rate increases nearly proportional to the flow rate up to about 1 mL$\cdot$h^{-1}, while in Region 2, beyond 10 mL$\cdot$h^{-1}, the leach rate is almost independent of flow rate. The steady-state concentrations of silicon, sodium, boron, and lithium at various leachate flow rates for SRL 131 glass are shown in Figure 5-10 (Hench et al., 1986).

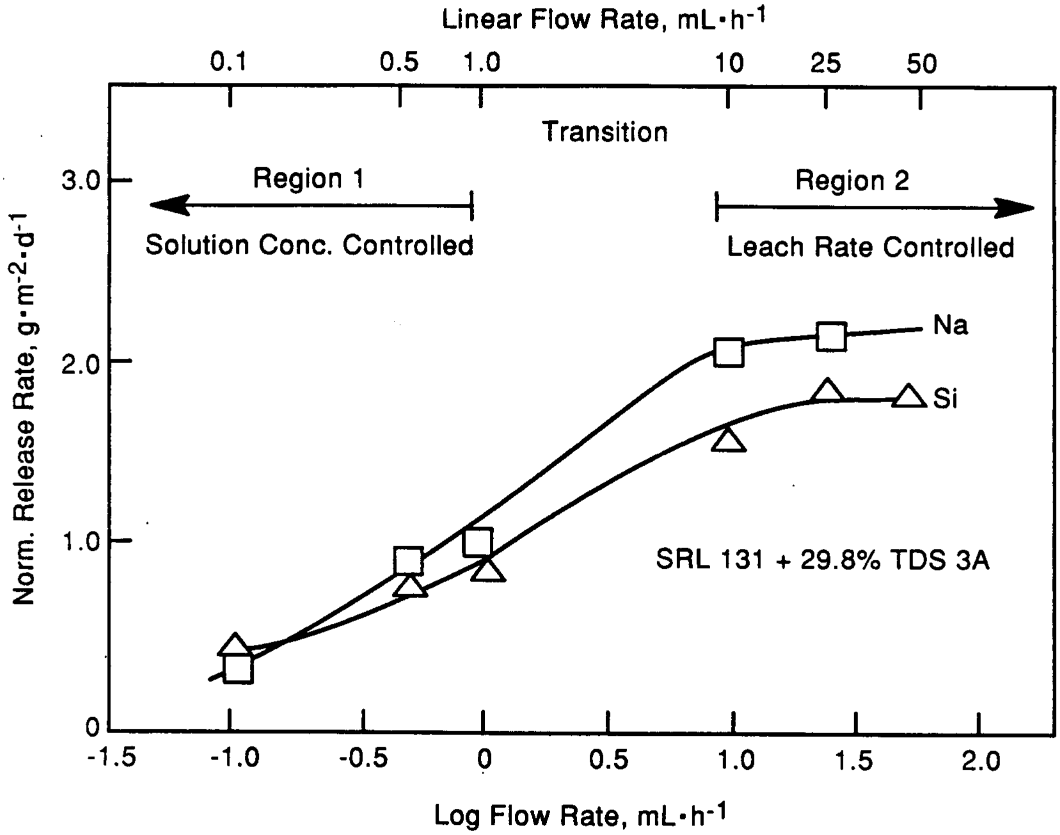


Figure 5-9. Normalized Release Rates of Sodium and Silicon as a Function of Leachant Flow Rates (Hench et al., 1986)

The results of flow experiments depend on the ratio of the total volume (V, m^3) of the leachant in the leaching cell to the flow rate (Q, m$^3\cdot$h^{-1}). The ratio V/Q determines the turnover time for one volume of the leachant in the leaching cell. Additionally, results in flow experiments depend on the glass surface area to the solution volume ratio. The higher the SA/V ratio, the faster the increase in the

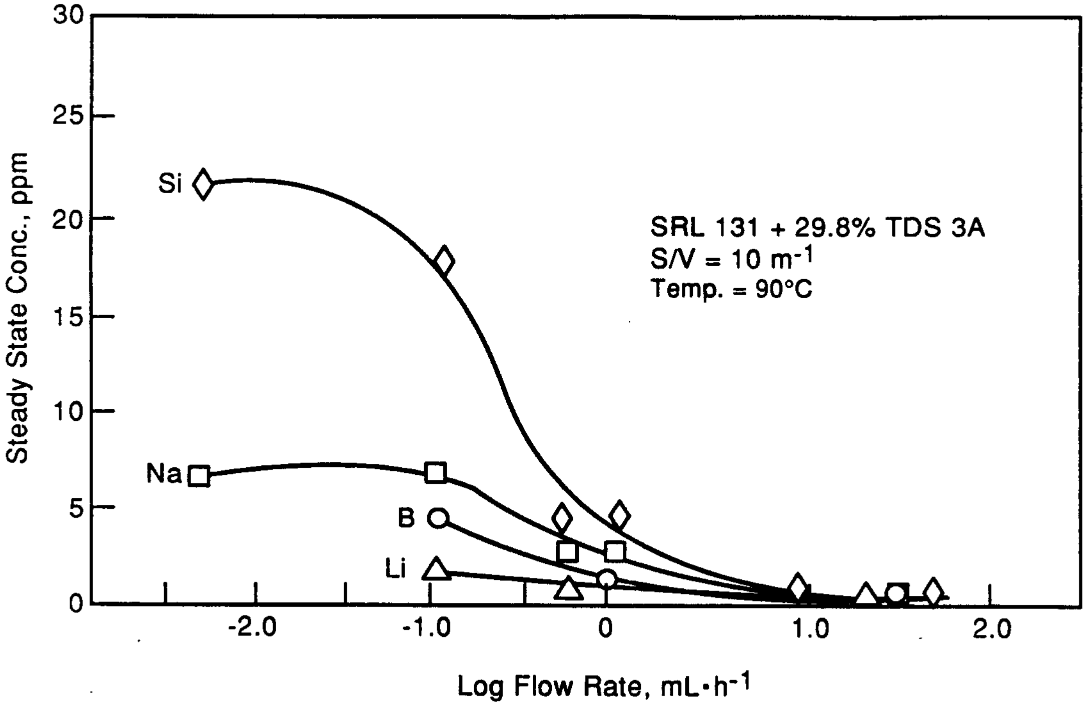


Figure 5-10. Effect of Flow Rate on Steady-State Concentration of Various Elements (Hench et al., 1986)

concentration of dissolved species in the leachate. Elemental release curves for SRL 131-type glass as a function of time and flow rate in deionized water at 90°C are shown in Figures 5-11(A) and (B) (Mendel, 1984). Figure 5-11(A) shows that the effect of flow is negligible at a flow rate of 0.1 mL•h^{-1}, with 60 mL total leachate volume and SA/V = 10 m^{-1}. The mass loss curve is practically identical to the one obtained in a static experiment as shown in Figure 5-11(A), lowest curve. The mass loss is approximately 10 g•m^{-2} after 14 days; thereafter, changing very slowly with time. On the other hand, at a flow rate of Q = 0.5 mL•h^{-1} with a 30-mL leaching cell volume, there is a measurable effect on the mass loss curve as shown by the second curve from the top in Figure 5-11(A). At Q = 1 mL•h^{-1} flow rate, a constant rate as shown in Figure 5-11(A), uppermost curve, is observed. Under this test condition, enough silica is being removed continuously from the leachate to maintain a relatively high corrosion rate. The rate is constant, as shown by the constant slope of the curve, because silicon cannot accumulate in the leachate. The total normalized mass loss at this flow rate is approximately 15 g•m^{-2} after 14 days, with a proportional increase thereafter. However, the flow rate has to be as high as 50 mL•h^{-1} for the corrosion rate to truly become independent of flow, as shown by the upper two curves for 100 mL•h^{-1} and 50 mL•h^{-1} in Figure 5-11(B) for SRL 131 glass. The corrosion rate has also reached its maximum value at this temperature. The total normalized mass loss as shown is approximately 35 g•m^{-2} after 14 days.

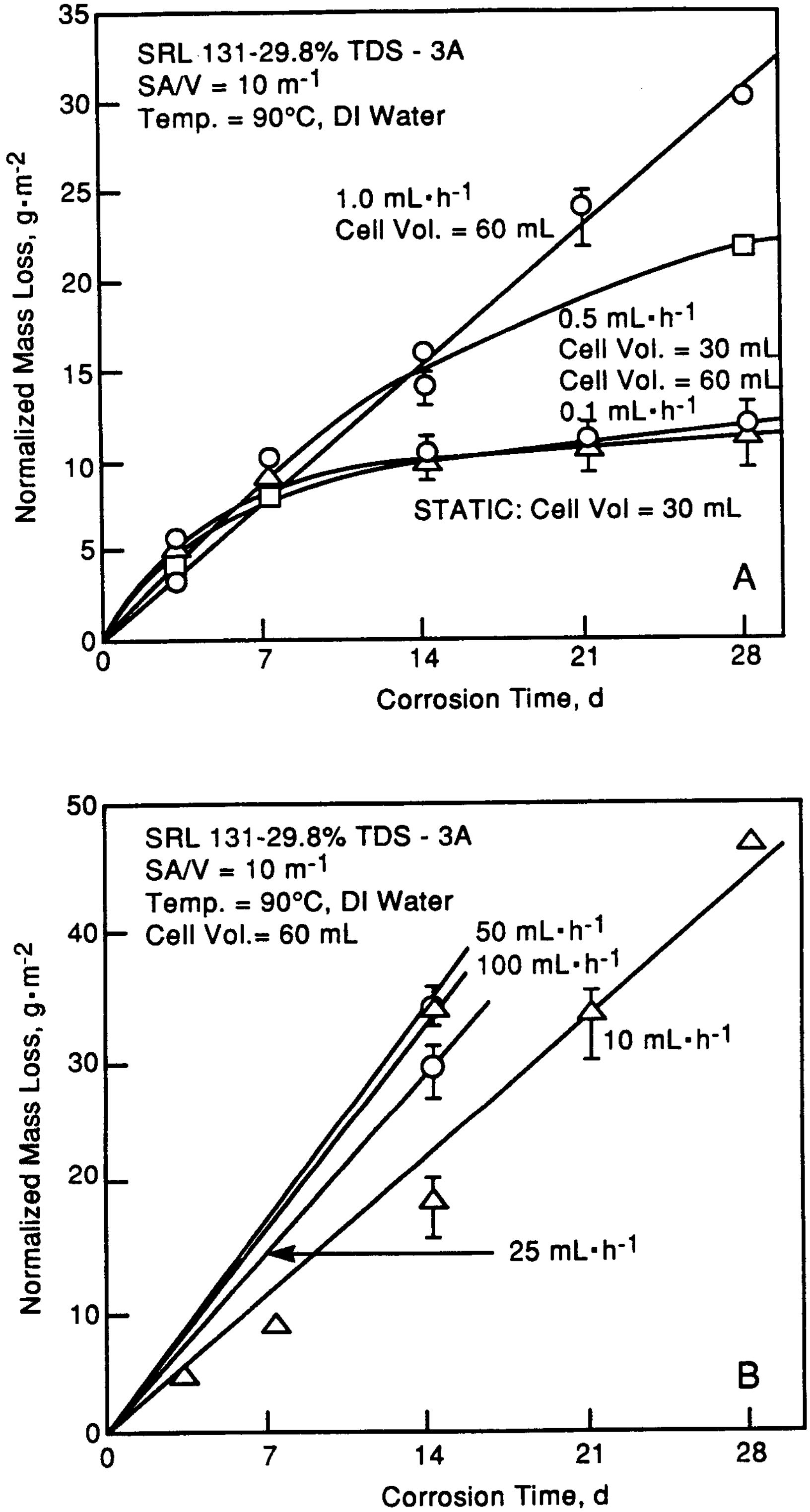


Figure 5-11. Normalized Mass Loss as a Function of Time and Flow Rate (Mendel, 1984)

5.6.3 Specimen Surface Area/Leachate Volume Scaling

In earlier literature, it has been suggested that glass leaching tests can be scaled by the product of SA/V ratio and the leaching test duration, namely, [(SA/V) • t, m^{-1} • d] product (Pederson et al., 1983). Based on this suggested scaling, leaching tests at various SA/V ratios should exhibit identical concentrations of the leached chemical species from the glass at equivalent [(SA/V) • t]. Other simple scaling factors, which supposedly produce a better correlation than the above scaling factor, have also been suggested (Grambow et al., 1988). However, there is no theoretical basis for such empirical scaling factors. In a recent investigation, leaching tests on two reference borosilicate glasses, namely, SRL 131A and SRL 202A, were conducted with SA/V ratios of 10 m^{-1}, 2,000 m^{-1}, and 20,000 m^{-1} (Ebert and Bates, 1992). The plots of the release of elemental boron as a function of the [(SA/V) • t] parameters for these two glasses are shown in Figure 5-12(A) and 5-12(B) (Ebert and Bates, 1992). The figures indicate

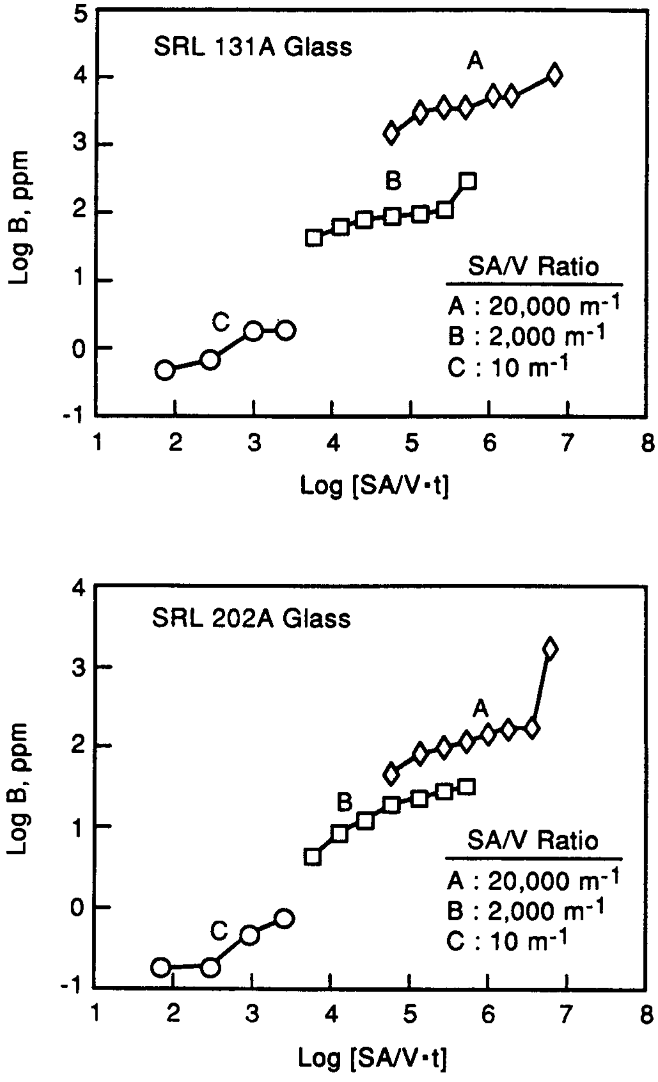


Figure 5-12. Release of Boron as a Function of [(SA/V) • t] Parameter for Three Widely Varying SA/V Ratios (Ebert and Bates, 1992)

clearly that the suggested scaling method is not valid. To the contrary, the data show that tests at higher SA/V ratios lead to higher releases from the glass. This observed trend is explained on the basis that leachate pH is higher for higher SA/V ratio tests for the same test duration (i.e., the leachate becomes chemically more aggressive in tests at higher SA/V ratio, leading to higher corrosion rate of the glass, and hence higher releases from the glass). The results indicate that a simple scaling method to predict long-term performance of glass from short-term experiments may not be valid due to chemical change in the leaching environment. Therefore, a mechanistic understanding of the glass reaction with the leachate is necessary in order to interpret tests at different SA/V ratios.

5.6.4 Closed versus Open System

The corrosion rate of glass in deionized water, in a closed system, is maximum in the beginning of the leaching test when the concentration of silica in the leachate is low. The observed rate decreases with time when the dissolved species accumulate in the leachate. Eventually, saturation with respect to one or more critical species would reduce the corrosion reaction (mass loss of the monolith) to a negligible rate. In contrast, at a low flow rate, a steady-state concentration in solution will be reached at which the corrosion reaction proceeds with a constant rate. Theoretically, the corrosion process is not expected to cease in an open system, because there is no equilibrium between the metastable glass phase and water. The critical glass corrosion rate-controlling species in solution is considered to be orthosilicic acid, H_4SiO_4.

5.6.5 Role of Surface Layers

In the course of the glass corrosion process, layers form on the surface of the monolith. There are various possible effects: (i) the layer could act as a diffusion barrier for either water transport to the reaction zone and/or transport of reaction products away from the reaction zone, (ii) the layer may have little or no effect on the transport of any critical species, or (iii) a passive layer may form on the glass surface. In case (i), the thickness of the layer should grow proportional to the square root of time, while in case (ii), the decrease of the corrosion rate would be expected, due to saturation effects in solution; that is, rate would depend not only on layer thickness but also on the kinetics of the solid reaction products which may form; and in case (iii), the rate is lowered as soon as a coherent layer forms.

As long as surface layers constitute no diffusion barrier for silicic acid (Pederson et al., 1983; Boult et al., 1979; Chick and Pederson, 1984), dependence of the corrosion rate with flow rate is maintained, and saturation effects of silica in solution will control the rate of reaction. However, in some cases, surface layers do constitute an effective transport barrier, as illustrated by the results of an experiment in Figure 5-13 (Werme and Grambow, 1987). The reaction rate, as indicated in the figure by the concentration of boron in solution, is not constant at a constant flow rate of 2.9 $mL \cdot d^{-1}$ used in the test, but decreases with time as the reaction layer grows. This example illustrates that it is important to know the influence of the surface layer on the corrosion kinetics for correct interpretation of the results of a flow experiment.

The features typically observed in surface layers of corroded borosilicate glasses are shown in Figure 5-14 (Mendel, 1984). The innermost layer, adjacent to the pristine glass, is the reaction zone typically less than 1 μm in thickness. This layer is generally depleted in soluble elements, such as boron, lithium, and sodium, and could exhibit extensive pitting. On top of the reaction zone is an altered layer with density in the range of 0.8 to 2 $g \cdot cm^{-3}$, compared to typical monolith glass density of 2.5 $g \cdot cm^{-3}$.

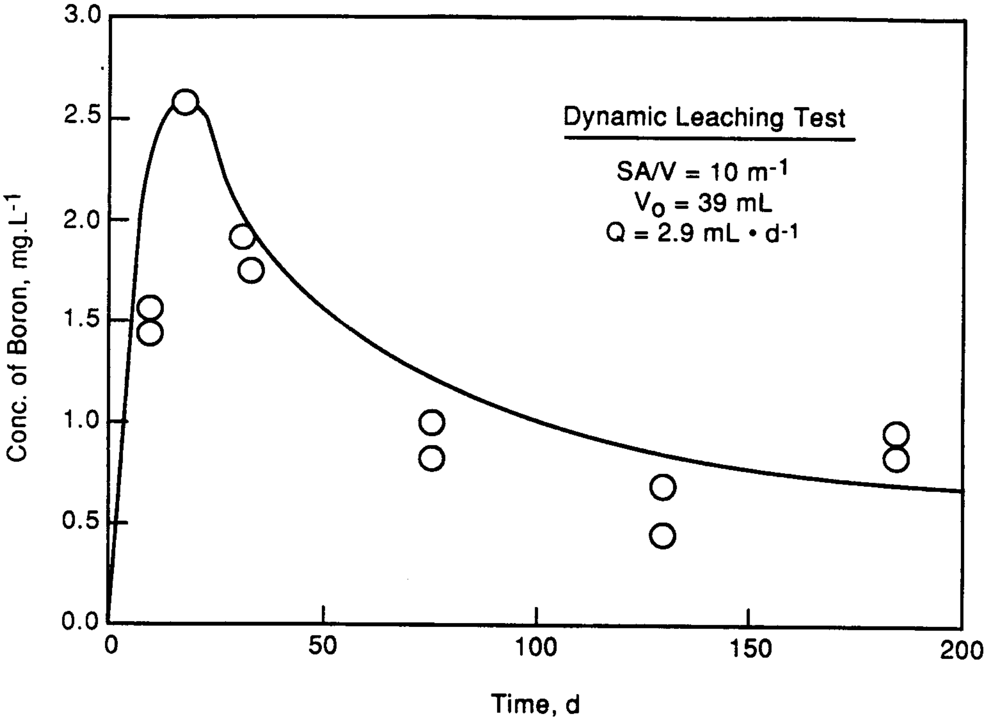


Figure 5-13. Boron Concentration in the Leachate as a Function of Time (Werme and Grambow, 1987)

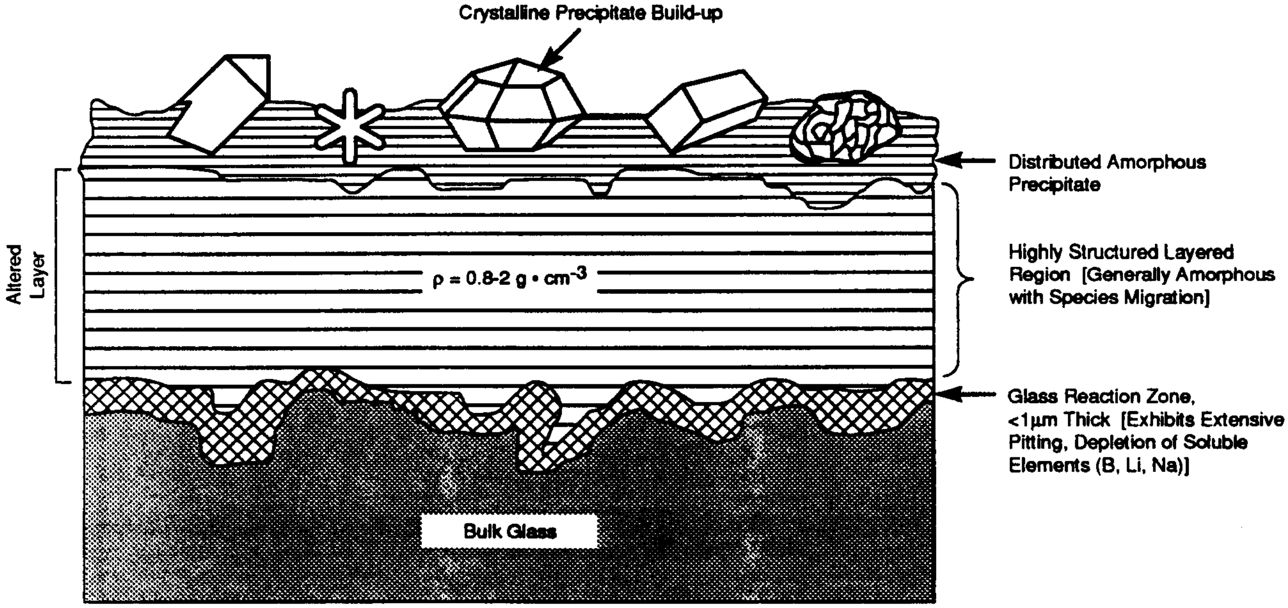


Figure 5-14. Features Observed in Surface Layers of Corroded Glass (Mendel, 1984)

This layer is porous enough to allow migration of reaction products outwards and water inwards. Layer thickness can vary in a wide range up to 100 μm and more, depending on temperature and exposure time of the glass to the test environment. In the outermost layer, which may be amorphous, crystalline precipitates may form. The kinetics of formation of crystalline phases, among other factors, depend on the wasteform characteristics and the SA/V ratio of the test set-up. The boundaries between the various layers are usually ill-defined, but the altered layer, together with the crystalline species, can be removed, leaving the reaction layer attached to the unaltered bulk glass.

Figure 5-15(a,b) (Lutze et al., 1983) shows features found on a borosilicate glass surface after corrosion in NaCl solution at 200°C. The figure shows an amorphous layer on the top, with the inner layer exhibiting drying cracks, while the outer layer shows different crystal morphologies. The cubes shown in this particular micrograph are analcime crystals ($NaAlSi_2O_6 \cdot H_2O$) which formed via a reaction between sodium in the leachate and silicon and aluminum released from the glass. Glasses have also been studied by exposing the samples to water vapor as opposed to liquid water at temperatures, ranging between 80 to 240°C (Bates et al., 1982). Some surface reaction products, such as analcime, were observed at all hydration temperatures on SRL 131 borosilicate glass, whereas other crystalline phases such as tobermorite, $Ca_5(OH)_2Si_6O_{16} \cdot 4H_2O$, were only present at higher temperatures, such as 240°C. The vapor hydration experimental conditions such as reported in the study resulted in a very high SA/V ratio, of the order of $10{,}000^{-1}$ m or even higher. This produced saturation of silica in the small amount of liquid phase present on the glass surface extremely fast. Additional comments on the effects of very high SA/V ratio are provided below.

Glass hydration (exposure to high temperature in limited amount of water) is considered to be an important scenario for an unsaturated repository. Thus, leaching studies on unaged (unhydrated) wasteform in liquid water might not adequately address the concerns related to the unsaturated repository (Bates et al., 1992). In a glass-aging (hydration) study, two borosilicate glasses, namely, type SRL 211 and SRL 131 glasses, were hydrated in steam in the 120°C to 240°C temperature range. The results indicated that humid atmosphere, like the aqueous environment, resulted in the formation of an altered surface layer which covered the glass with crystalline mineral phases. The hydrated layer consisted of a thicker inner layer that was nearly depleted of sodium and partially depleted of aluminum and calcium and a thinner outer layer believed to be montmorillonite-type clay. The thicker layer was cracked. Although the crack dimensions and morphological features may not exactly reproduce those that might be expected to form during the period prior to liquid water coming in contact with wasteform in a geological repository, almost any type of cracking of the layers would expose the pristine glass to attack by water present in the repository. Such a layer cracking phenomena is likely to accelerate leaching of radionuclides from the wasteform. Figure 5-16 (Bates et al., 1982) shows a sequence of SRL 131 borosilicate glass hydration at 202°C for 6 hours to 14 days. Several different crystal species were observed on the glass surface, with the entire surface covered with a white fibrous layer after only 14 days of exposure. The trapezohedral crystals were identified as analcime, $NaAlSi_2O_6 \cdot H_2O$. Individual crystals up to 100 μm in size were reported. The fibrous mineral shown in the figure was identified as tobermorite, $Ca_5(OH)_2Si_6O_{16} \cdot 4H_2O$, which is one of the main constituents of concrete. The bulk glass surface was transformed into a secondary crystalline layer up to 5 μm thick. This mineral layer was not identified unambiguously but is believed to belong to montmorillonite-type clay. A significant conclusion drawn from the investigation was that hydration of HLW glasses can occur very rapidly even at moderate temperatures which are likely to be encountered by the wasteform in a geological repository (U.S. DOE, 1988). Based on the experimental investigation, it is apparent that glass surfaces could be significantly altered during the supposedly (hydraulically) dry period with no resultant release of radionuclides from the wasteform due to the absence of a transport medium. However, subsequent contact of the hydrated

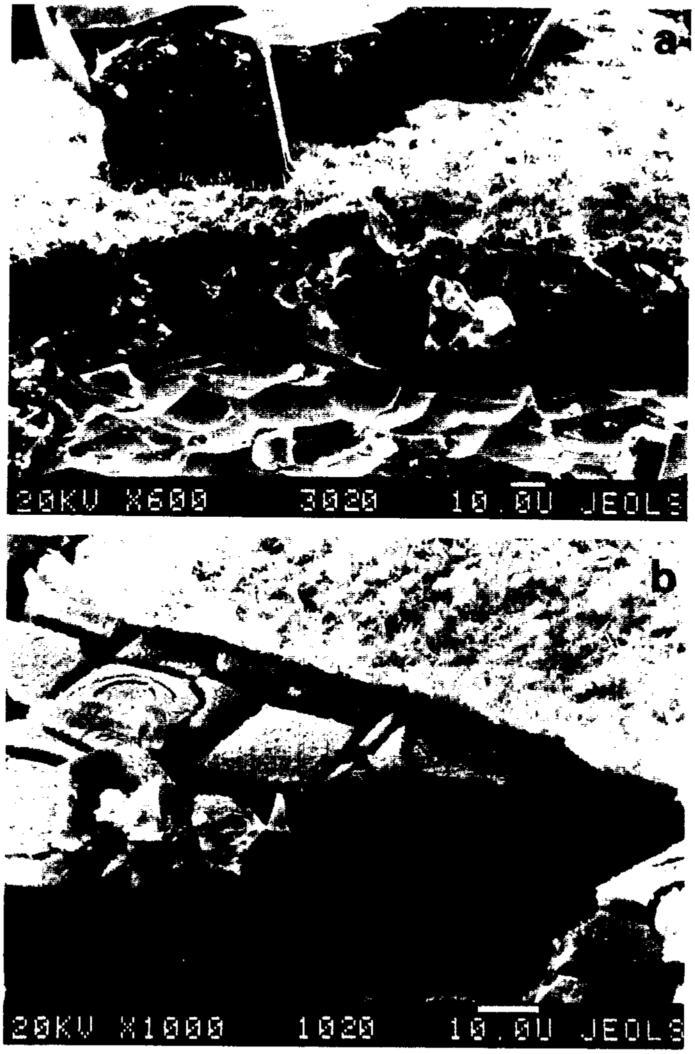


Figure 5-15(a,b). Surface Layer Morphology on the Borosilicate Glass C31-3 EC Corroded at 200°C for 30 Days in NaCl Solution (Lutze et al., 1983)

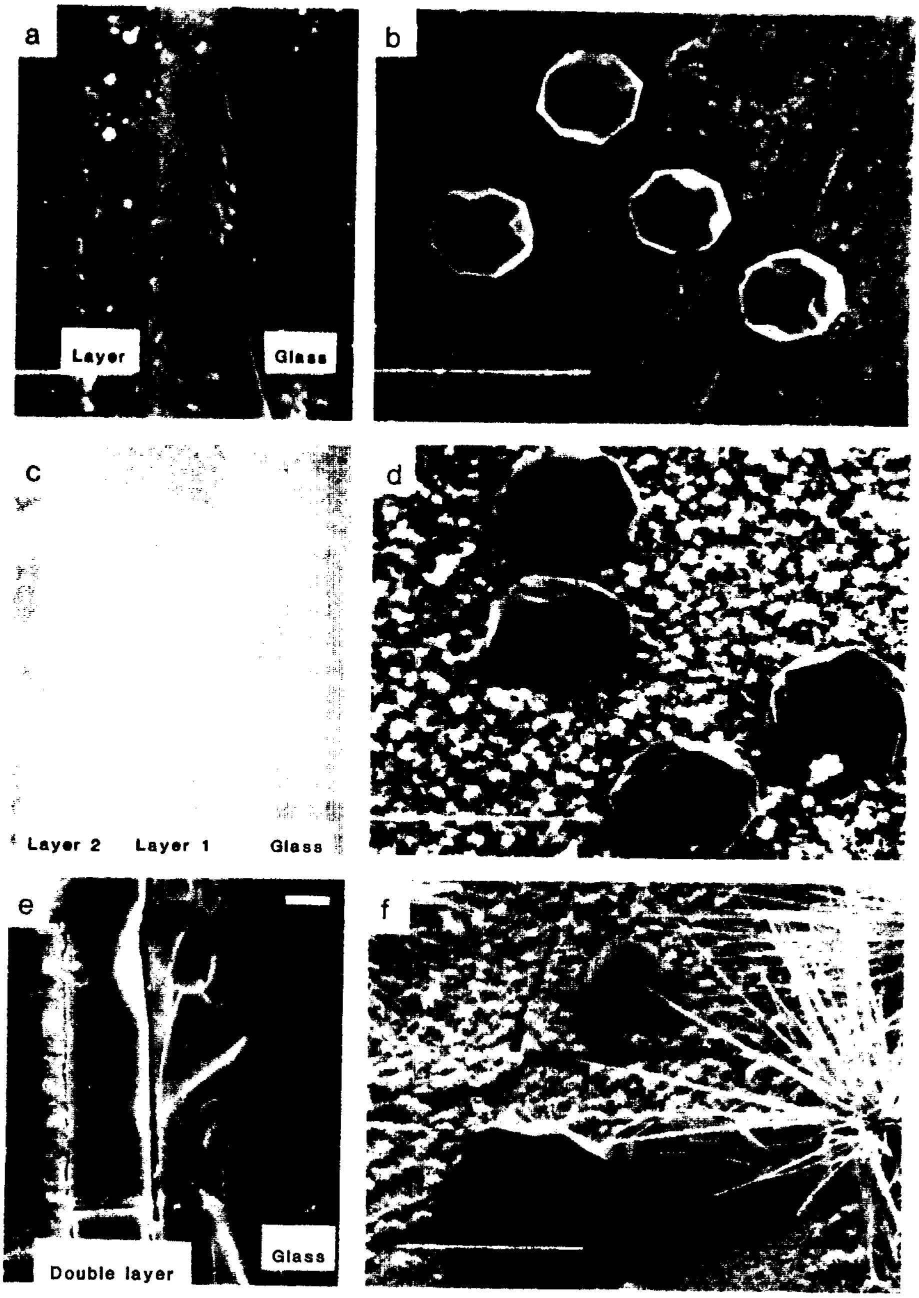


Figure 5-16. A Series of SEM Photomicrographs of Hydrated (202°C) SRL 131 Glass: (a) Cross Section Showing a Single Hydrated Layer, 6 Hours Exposure, Scale = 5 μm; (b) Surface Showing Analcime Formation, 6 Hours, Scale = 50 μm; (c) Cross Section Showing a Double-Layer Formation, 24 Hours, Scale = 5 μm; (d) Surface Showing Analcime Formation and Surface Alteration, 24 Hours, Scale = 50 μm; (e) Cross Section Showing Advanced Double-Layer Formation, 192 Hours, Scale = 8.5 μm; and (f) Surface Showing Analcime and Tobermorite Formation, 192 Hours, Scale = 95 μm (Bates, et al., 1982)

glass with repository waters could produce very different release characteristics as compared to those from unaged glass under hydrothermal conditions. Therefore, the alteration of the glass surface in a steam environment, and the consequences of such alteration on the long-term performance of the wasteform, cannot be inferred from leaching tests in liquid water both in terms of the types of mineral phase formation and the reaction kinetics. Since the possibility of the glass wasteform being exposed to high temperature vapor phase for possibly decades to hundreds of years prior to exposure to liquid water exists in a geological repository, there is a need to better understand radionuclide release characteristics of hydrated HLW glasses.

5.6.6 Very High Wasteform Surface Area/Leachant Volume Ratio

In an attempt to simulate more realistic repository conditions in a hydraulically unsaturated geology, limited experiments have been performed with very high glass surface area to liquid volume (SA/V) ratios, such as 4,000 m^{-1} (Ebert and Bates, 1992). Such studies were conducted in a hydrated steam environment at 200°C. Control experiments were performed in liquid water with SA/V of 40 m^{-1} for comparison. The conclusions of the investigators (Ebert and Bates, 1992) can be summarized as:

- Solid reaction layers are formed on the outer surfaces of the glass in both steam and liquid water environments. Solubility constraints limit the concentrations of most species in solution and the reaction layers are enriched in insoluble species. Secondary phases formed during the reaction of glass with steam may reduce the amounts of species with low solubilities in the layers. These species do not accumulate in the layer in the steam environment but do accumulate in the layer in the liquid environment where precipitates have not formed.

- The low residual rate of glass reaction approached in static leach tests at low SA/V ratios cannot be used to project the glass reaction rate to long reaction times if precipitates form. The rate of glass reaction may be much greater than the residual rate when precipitates form and may vary with the types of secondary phases formed. Silicon-containing phases probably have the greatest effect on the reaction of borosilicate glasses.

- The assemblage of precipitates observed in the experiments using high SA/V ratios are not well predicted by the widely used geochemical codes, such as EQ3/6. This is attributed mainly to the incomplete databases used in the simulation and to the possibility that the most stable precipitates are not always formed in the experiments. Thus, the experiments in steam provide a simple means of identifying those precipitates which actually form, and it is suggested that these should be added to the databases.

- Reactions in steam are greatly accelerated relative to reactions in liquid water, in the sense that higher solution concentrations are attained after very little glass has reacted. Nucleation energy barriers may be overcome after only a few days of reaction in the steam environment, and secondary phases may precipitate and establish lower solubility limits for major glass components to maintain a high reaction affinity.

It is reported that reactions in steam and in liquid water can be compared using SA/V ratio considerations prior to the solution becoming concentrated in species released from the glass and prior to precipitate formation. Acceleration of the reaction upon precipitate formation, however, complicates the comparison, because material released from the glass may either enter the solution or form secondary phases depending on a number of factors which are not fully understood as yet.

5.6.7 Effects of Colloids

Colloids can form when glass wasteforms are leached in pure water alone. However, the observable concentrations of colloids are much higher when glass is leached in the presence of iron. Studies on the effects of iron on glass leaching have led to the conclusion that increase in the leaching rates are due to changes in the redox potential (Eh). Under aerated conditions, Fe^{2+} is produced which drives the Eh into a region of stability for ion silicate, forming either as precipitate or colloids. Oxygen is required for the dissolution of Fe^{2+} which then scavenges silica from the solution, resulting in undersaturation of silica and hence more dissolution of the glass. The formation of colloids is minimal under anoxic conditions due to the limited supply of Fe^{2+} in solution. It has also been reported that concentrations of plutonium, neptunium, uranium, and strontium are observed to be enhanced in unfiltered leachant containing iron (Ringwood and Kelly, 1986). These particular elements appear to be incorporated into filterable colloids, since their concentrations were less after filtering. Both the size and composition of these colloids appear to be variable. As mentioned in an earlier section, a number of other actinides may also be redox sensitive, and they may also form colloids or precipitates. Such forms of release from the glass monolith into the leachate could have an influence on the corrosion kinetics of the glass and transport of the radionuclides to the repository far-field. In a recent study on the colloid formation during borosilicate wasteform interaction with limited amount of water (simulating hydraulically unsaturated repository condition), it has been reported that nearly 100 percent of the total plutonium and americium in the leachate were concentrated in submicrometer-size colloidal particles (Bates et al., 1992). The investigation concluded that models of actinide mobility and repository integrity, which assume complete solubility of actinides in groundwater, underestimate the potential for radionuclide release into the environment. It has been suggested that a colloid-trapping mechanism may be necessary for waste repository to meet long-term performance requirements (U.S. NRC, 1992).

Although it is generally agreed that an understanding of the phenomenon of colloid formation and precipitation requires information related to the redox potential of the repository environment, types and amounts of ionic species released from the waste-package components, the temperature of the environment, residence time of the leachant (volume changes), and perhaps other parameters, it is also generally believed that their impact on glass HLW degradation under repository environment is currently not fully understood. Mechanistic understanding of the glass corrosion phenomenon essential to long-term performance modeling would require analysis of the leachate containing dissolved constituents from the glass beyond the surface layer; analyses of the type, characteristics, and sizes of colloids and precipitates in the leachate; and the characteristics and properties of the reaction products in the surface layers. An increased effort in investigating the role of colloids and precipitates in the degradation of the glass wasteform is suggested.

5.6.8 Effect of Radiation

Radiation can affect the release rate of radionuclides from HLW glasses by increasing the surface area due to microfracturing and/or by changing its microstructure, leading to increased dissolution rate in groundwater. The extent of the radiation-induced microfracturing will depend on differential volume change, development of new microstructure, and mechanical properties of the radiation-damaged glass. At the present, there is insufficient data and understanding to predict the extent of radiation-induced microfracturing in HLW glasses. Almost all data on the effects of α-decay on dissolution rates of HLW glasses were generated in short-term tests based mainly on mass loss of the glass monoliths. The representative data obtained from such tests, shown in Figure 5-17 (Weber, 1991), indicates less than a factor of 3 increase in the short-term dissolution rates. However, it has been established that short-term tests based on mass loss can underestimate the radiation-induced increases in dissolution rate by a factor of 3 to 4 (Weber, 1988; Westsik and Harvey, 1981). Therefore, a conservative estimate would be an increase of up to an order of magnitude in the corrosion rate of borosilicate glasses. Any adverse temperature dependence of the radiation effects would further increase the dissolution rate of glass at high temperatures.

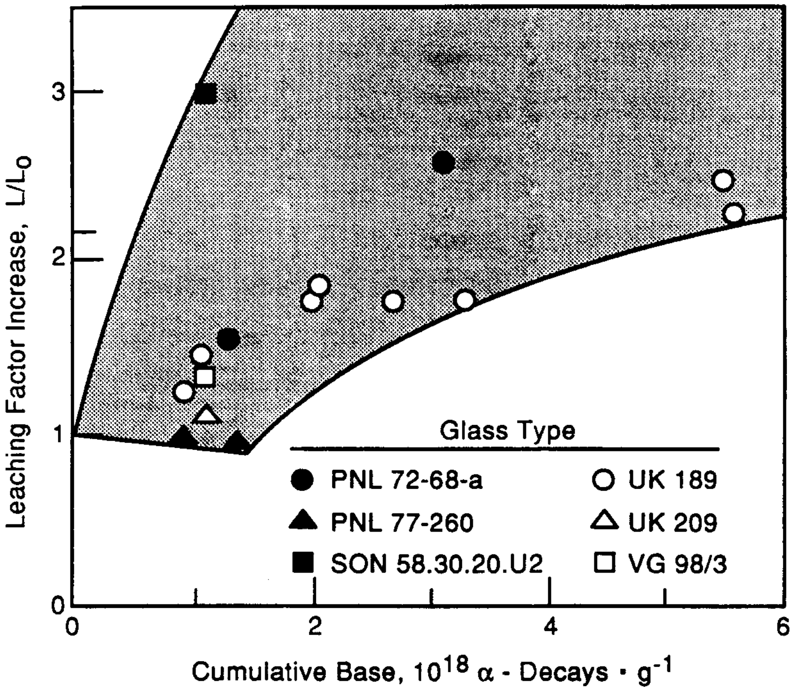


Figure 5-17. Increase in Leaching Factor (L/L_o) as a Function of Radiation Dose for Short-Term Tests (Weber, 1991)

5.6.9 Ion-Irradiation/Neutron Irradiation/Gamma Irradiation

Ion-irradiation and neutron-irradiation studies of several HLW glasses have shown that irradiation enhances the dissolution rates in aqueous media of up to a factor of 4 (Dran et al., 1980; Primak, 1982; Cousens and Myhra, 1983). Ion-irradiation is also known to introduce composition variations in glass (Arnold et al., 1985), which make the changes in the leach rates difficult to interpret. Gamma irradiation of several HLW glasses with doses of up to 10^{11} rad have also shown increases in dissolution rates of up to a factor of 4 (Bibler and Kelley, 1978; Grover, 1973). It should be noted that the dissolution rates are generally measured by the total mass loss of the specimen; as such, they may not be a true indicator of any specific radionuclide release or its surrogate in glasses containing simulated wastes. Actually, very few studies have been performed on glasses containing radioactive wastes. Therefore, generally accepted maximum enhancement of a factor of 4 in the leach rates due to ion-, neutron-, and gamma-radiation needs to be validated for highly soluble elements, such as boron, lithium, and sodium, in glasses containing radioactive wastes.

5.6.10 Ion-Implantation Versus Actinide-Doping

The ion-implantation technique has been used to accumulate high irradiation doses in short periods of time to study dose and dose rate effects or the effect of different atomic masses and energies on the chemical durability of HLW glasses. Glasses irradiated with 200 keV Pb ions and corrosion tested in aqueous solution have exhibited a critical dose of 5×10^{12} ions$\cdot$cm^{-2}, above which the chemical durability of HLW glasses decreased drastically, viz., by a factor of 20 or more (Arnold, 1985; Dran et al., 1980). The existence of a critical dose has been explained as the value at which individual damage zones from the penetrating particles overlap to form a homogeneously damaged material. The observation of this critical dose raised some concerns about the appropriateness of heavy ion implantation as a simulation technique to study radiation effects on HLW glasses. The difference in densities of irradiated glasses and number of displaced atoms have been used to explain small differences, such as a factor of 3 or less, between corrosion rates of ion-irradiated and actinide-doped glasses. However, larger increases, such as 20 times or more, have never been observed in actinide-doped HLW glasses as sometimes observed in ion-implanted glasses. There is no drastic enhancement of the corrosion rate at any dose for actinide-doped glasses and, thus, no identifiable critical dose. A possible explanation provided for the large difference between the leach test results of ion-implanted versus actinide-doped samples is the contribution of the thermal annealing process, which is believed to be much more effective in actinide-doped glasses versus ion-implanted glasses in mitigating the affect of radiation damage on the leaching of glass.

5.6.11 Effects of Leachate Radiolysis

Aqueous solutions are exposed to ionizing radiation when in contact with radioactive waste, leading to radiolysis (i.e., radiation-induced decomposition of water or vapors). The short-term dose rate is determined by β- and γ-radiation, while the long-term dose rate is controlled by α-radiation. The thin wasteform metal container would be penetrated by γ-radiation leading to radiolysis of water, if water were present in the repository. Such a situation would have an adverse effect on the container corrosion resistance. The other types of radiation, namely, β and α, would be too weak to penetrate the container walls; therefore, the radiolysis of water or vapors in the vicinity of the waste package is only possible if the wasteform comes in direct contact with water through a breached container. Such a possibility is remote if the container remains intact for the required period of 1,000 years after the repository closure (U.S. NRC, 1992).

The typical radiolytic products of water and their G values (average number of radiolytically generated or destroyed species per 100 eV of absorbed radiation energy) are listed in Table 5-1 (Lutze and Ewing, 1988). The primary products e_{aq}^-, H^+, H, H_2, OH^-, HO_2, H_2O_2 are involved in a number of secondary chemical reactions and new species, such as the molecular anion O_2^- and molecular oxygen, are formed. Eventually, a dynamic equilibrium is established between water which is radiolytically decomposed and that which is reformed by recombination reactions. The concentrations of the various radiolytic species depend on temperature and pressure, type of radiation (α or γ), dose rate, and the presence of impurities. If a gas phase is present, such as oxygen and/or nitrogen, it is also subject to decomposition/radiolytic reactions. NO_x can form and then dissolve in water, leading to the production of nitric acid. The radiolytically formed species and the relative concentration in the solution have been shown to influence the glass corrosion rate or the process.

Table 5-1. Primary Radiolytic Species and their G Values for γ- and α-Radiation (Lutze and Ewing, 1988)

Species →	e_{aq}	H^+	H	H_2	OH	HO_2	H_2O_2	H_2O
γ	2.7	2.7	0.6	0.43	2.86	0.03	0.61	−4.14
5 MeV α	0.3	0.3	0.3	1.4	0.5	0.10	1.3	−3.3

Experimental studies have been conducted to measure corrosion rates of PNL 76-68 glass samples under external γ-source, at a dose rate of 2.4 $Mrad \cdot h^{-1}$ (McVay and Pederson, 1981; McVay et al., 1981). (Note: This dose rate is at least an order of magnitude higher than that expected from the high-level glass wasteform.) From the results obtained, the following conclusions have been made: (i) irradiation of the glass alone does not affect its chemical durability, (ii) irradiation during corrosion in the presence of air does have an effect (release rates were increased by a factor of 4 to 6), (iii) irradiation during corrosion with air excluded has a much smaller effect than when air is present, and (iv) the effect of γ-irradiation on aqueous corrosion is more pronounced at 90°C than at 50°C (McVay et al., 1981). In another glass-leaching experiment, it is reported that irradiation in the presence of air generated nitric acid, leading to lower pH value of the solution (decrease from 5.7 to 3.3) (Yokoyama et al., 1985). This resulted in an increase in the concentrations of zinc and neodymium in solution because of their higher solubility at low pH. These elements would otherwise have precipitated on the glass surface. Since actinides also have pH dependencies similar to neodymium, radiolysis in the presence of air would increase their concentrations in solution also, and hence increase their susceptibility to transport to the repository far-field.

In another study on behavior of actinide-doped SRL 165 and PNL 76-68 glasses subjected to γ-radiation in a saturated tuff environment for exposure times ranging up to 56 days at 90°C with a dose rate of 2×10^5 $rad \cdot h^{-1}$, the following general conclusions were made (Bates and Oversby, 1985): (i) the parameters that control the reaction of glass with water are dependent on the dynamically occurring processes of glass dissolution and nitric acid generation. Anything that artificially upsets this balance will unnaturally affect the degree of reaction. Thus, if a γ-field larger than expected in the repository is used to accelerate the reaction, the actual effect may be to alter the mechanisms by which the glass reacts. Nitric acid generation, via the radiolysis of nitrogen/air, would be accelerated by the larger dose rate, and this may overcome the glass buffering capacity and cause dissolution of selected glass constituents that might not occur with lower dose rates; (ii) alternatively, γ-irradiation tests conducted using deionized water as the starting solution with an initial pH of typically 5 to 7 would become more acidic very quickly. This may introduce pH conditions that would not be attained using actual repository radiation dose rates and repository waters, thereby creating conditions which would artificially influence (could increase) glass leaching. Hence, the radiolytic products of repository gases could also have a profound influence on the degradation of glass wasteform. The less durable glasses which are likely to release greater amount of alkalies may buffer the radiolysis of nitrogen which would have otherwise lowered the pH of the leachate leading to enhanced attack on the silica network of the wasteform. The effects of increased dose rate may also lead to changes in the mechanism of glass degradation depending on the test conditions. Therefore, the experimental test condition should be carefully factored into any extrapolation of results for predicting long-term performance.

5.6.12 Unsaturated Environment Studies

Although the repository site being considered in the U.S. is hydrologically unsaturated, few experimental investigations have been conducted under such conditions. One such study was conducted specifically to evaluate the effects of radiation under unsaturated conditions representative of the environment expected at the repository site. The investigation used specimens of SRL 202 frit based glass doped with the transuranic isotopes ^{237}Np, ^{239}Pu, and ^{241}Am and a uranium-containing analog (Bates and Oversby, 1985). The experiment was set up to evaluate the effects of both γ- and α-irradiation on high gas/liquid environments and then examine the influence of radiation on the alteration of glass and formation of secondary mineral phases. The SRL 202 glass was exposed to an external gamma radiation field of 3.6×10^3 rad$\cdot$h^{-1} and an alpha field (from the glass) of approximately 100 rad$\cdot$h^{-1}.

The results show that glasses reacted to form discrete secondary phases after exposure of only 7 days. After 35 days of reaction, the secondary phases observed included analcime, weeksite, and tobermorite. Between 35 and 65 days, the reaction progressed completely through the 2-mm thick specimen, and segments of the reacted surface had fallen to the bottom of the leaching vessel. The SRL 202U glass was hydrated under identical conditions but without radiation exposure. Tests on this glass also ran from seven to 65 days. In this sample, no unique secondary phases nucleated, but instead, a hygroscopic salt-rich film formed on the glass surface. The following general conclusions have been drawn from these experiments (Bates and Oversby, 1985; Wronkiewicz et al., 1991):

- Blank experiments indicate that radiolysis products are concentrated in the thin films of water that condense on solid components in an unsaturated test environment

- Amount of nitrate and nitrite produced in the alpha blank tests is consistent with that expected and had a yield of G(NO_x) ~2 molecules per 100 eV

- Radiolytic products may form nitric acid with a resultant pH decrease of the solution in contact with the samples

- Faster glass alteration rates are observed in an irradiated vapor phase environment as evidenced by the greater thickness of the reacted layer and abundance of secondary phases on the glass surface

- The assemblage of secondary phases that precipitate in the irradiated environment appear to be different from those formed in nonirradiated environments

The cause of the accelerated reaction under irradiated conditions and the exact radiolytic products responsible for the glass reaction had not been established (Wronkiewicz et al., 1991). However, it is important to note that the radiation field used in the test was several orders of magnitude greater than that would be expected in a geological repository; as a result, some of the observations and their consequences may not be fully applicable to lower levels of radiation likely to be encountered in the actual geological repository.

6 GLASS CORROSION MODELING

As a prerequisite to developing a robust performance predictive model for the HLW borosilicate glass, the mechanistic behavior and quantitative information related to the materials properties of the wasteform and its response to the anticipated repository geochemical environment need to be incorporated into mathematical formulations. Such a task is not easy for a number of reasons: most studies to date have been related to investigations of a single parameter or material property; the database is mostly based on short-term experiments; the laboratory test conditions are not directly relatable to the geological repository environment/conditions (e.g., most leaching studies have been conducted in static, deionized water, in closed systems); and there is an element of uncertainty about the repository environment and geochemical parameters. Nevertheless, leaching models are being developed for long-term performance predictions of wasteforms in a repository. The available models are simple and limited in their capabilities. The validation of such models generally comes from laboratory tests which are appropriate only for rank ordering different types of wasteforms. Generalized models with theoretical foundations for long-term performance assessment are not available as yet. Although a review of the available models is outside the scope of this report, a very brief overview of the progressive development in glass wasteform modeling is provided below.

Prior to the detailed investigation of HLW glass corrosion in the past two decades, the reaction of glass with water was explained by a combination of diffusion and dissolution phenomenon. The early part of the reaction in borosilicate glasses was considered controlled by Na^+/H^+ ion exchange. Such a hypothesis was supported by the observed variation in the glass corrosion rate with $1/t^{1/2}$ dependence, followed by matrix dissolution. Further progress in the understanding of glass degradation led to the incorporation of combined transport (solid state diffusion) and surface processes (solubility coefficients, rate constants and mass transfer coefficients) (Machiels and Pescatore, 1981). Quantitative support for this approach was provided by successful fits of experimental data from leachant flow tests. However, no independent measurements of the materials constants of the wasteform were available in order to test the model under conditions other than those of data acquisition. Further, refinement to the modeling capability led to the consideration of the accumulation of dissolved species in limited volumes of leachate (Harvey and Jensen, 1982). In such models, readsorption of dissolved species on the glass surface was assumed; however, the formation of solid crystalline phases was neglected.

Progressive development in glass degradation modeling led to a type of model which considered many more observed characteristics of the borosilicate glasses than before. Examples include: existence of a constant and maximum corrosion rate at infinite dilution and constant temperature and pH, dependence of the corrosion rate on flow rate, existence of a silica saturation concentration in a closed system, formation of surface layer, and the effect of surface layer on the corrosion rate. In this type of model, it was assumed that the rate of dissolution of silica from the glass per unit of surface area was the same as the diffusion rate of silica through the precipitated surface layer into the leachate. Through the application of this mechanistic approach, expressions for two rate-limiting cases were developed: (i) transport of silica across the surface layer and (ii) dissolution of silica (Wallace and Wicks, 1983). This type of model predicts that the slope of the leaching rate as a function of time is 1 in the beginning of the corrosion process, rather than 1/2 as predicted by pure diffusion models, and that it approaches 1/2 as layer thickness increases (Wallace and Wicks, 1983). It is stated that this slope is expected to be maintained in an infinite solution volume or will decrease to zero in a limited volume of leachant (because of saturation effects). If the leachant volume is small enough, saturation may be reached before diffusion can be identified as a rate-limiting process. Such a case would develop if very high SA/V ratios were used. The limitation of this type of model is that the corrosion reaction ceases at silica saturation and that there is no explanation for experimentally observed glass corrosion over long periods of time, albeit at a low rate, even after the leachate is saturated in silica (Grambow, 1985; Freude et al., 1985; Wicks et al., 1986).

Improved nexus between experimental observations and theory is provided by a more advanced model which, in addition to the parameters incorporated in previous models, takes into account the effect of the formation of surface layers on corrosion rate and also the fact that corrosion of glass continues at a slow but measurable rate even after apparent saturation of the aqueous solution with silica (Grambow, 1985; Grambow et al., 1987; Grambow, 1983). Such a model uses a general rate equation for glass dissolution. The rate-limiting step in this type of model is the decay of an activated H_2SiO_4 complex on the glass surface. The leachant saturation term involves only the glass surface, and soluble elements can still be released upon hydration of the bulk glass beneath the surface layers. Experimentally-measured rates after silica saturation are much smaller than the forward reaction, and rates as low as between 1/6 to 1/1,000 of the forward rate, depending upon the type of glass and experimental conditions of temperature, leachate composition, and presence or absence of backfill material or container corrosion products, have been reported (Grambow et al., 1988; Lutze et al., 1988). All kinetic input data for exercising such a model have to be experimentally determined, except for the diffusion coefficient of silica in the surface layer which is adjusted to fit the data. Comparison of experimentally observed corrosion/leaching rates with those predicted by such a model reportedly are within 30 percent for solution concentrations of soluble elements. Predictions for solution concentrations of elements in the precipitated phases are reported to be much less accurate. These uncertainties in calculated concentrations of the less soluble elements are the result of inability of the model/code to accurately determine the formation of the type of crystalline phases, particularly the metastable phases for which thermodynamic data are currently unavailable in the geochemical codes, such as PHREEQE or EQ3/6. Therefore, there is a need for inclusion of the observed crystalline phases, from experimental investigations and their thermodynamic data particularly at high temperature, in the geochemical databases. This would help relate the results of the model better to the observed alterations of the glass and will increase the accuracy of the model in predicting long-term releases under varying environmental conditions that could be expected in a geological repository. Effects of the radiation (radiolysis of vapor, gases, and groundwater) could be incorporated by changing the chemical composition of the leachate as functions of radiation dose and time.

7 CONCLUSIONS AND IDENTIFICATION OF REPOSITORY RELATED ISSUES

The accuracy of the mathematical models for predicting the performance of the borosilicate HLW wasteforms depend on the relevance and precision of the experimental data used in developing and validating the models. Extensive experimental investigations have been conducted over the years to understand the degradation mechanisms of the wasteform. The data and information generated through such laboratory experiments provide insight into the characteristics of the glass wasteform and its likely degradation modes under the test conditions. In many cases, the test results raised additional concerns/ issues. Based on the literature, it is concluded that the following areas require generation of additional information/data for evaluating performance of borosilicate glass wasteform in a geological repository. In conducting additional experiments, the goal should be to generate an adequate database for building a robust model and for validating the model to predict the performance of the glass wasteform under repository specific conditions for a period of 10,000 years. The depth to which each of the following areas need to be investigated further will be dictated by the needs of resolving assumptions made in developing and exercising glass degradation as well as overall systems performance models for determining the releases in the wasteform near-field and repository far-field, to demonstrate compliance with the federal regulations (U.S. NRC, 1992).

- Eh/pH

  Many elements in wasteform and waste package are likely to occur in variable oxidation states. Also, the composition and solubility of many species derived from these elements are dependent on pH. Therefore, it is important to understand the effects of potential and pH on oxidation states of elements that occur in more than one oxidation state. The elements in wasteforms that can be affected by changes in redox conditions and which are of particular interest include tecnicium, uranium, and other actinides.

- SA/V Ratio Related Effects

  The ratio of the wasteform surface area to solution volume is an important parameter that affects both dissolution and precipitation kinetics. It becomes an issue in test methods using powdered wasteform, such as the recently developed PCT, to measure its chemical durability (since this particular test method does not specify the SA/V ratio as a test parameter directly). The SA/V ratio is one of the primary terms that could allow scaling of data from small samples to the full-scale wasteform monolith. The information of SA/V, including particle size and characteristics, could possibly be related to the releases from the monolith.

- Waste Package Material Effects

  Corrosion products and release of ionic species from the waste package materials can influence the dissolution behavior of borosilicate glass wasteform [e.g., corrosion products could change (reduce) the pH of the water present in the vicinity of the wasteform leading to accelerated degradation of the glass network]. The corrosion products released from the waste package components could also contribute additional quantities and types of ionic species to the near-field which may influence surface layer formation (secondary mineral formation on the surface of the wasteform) which may or may not be protective in nature.

Therefore, the degradation of the glass wasteform should be studied in conjunction with the degradation of other materials likely to be in the vicinity, the waste container being one major component. For example, the discussion earlier has shown that the presence of iron in the leachate could have a deleterious effect on borosilicate glass degradation in aqueous environment via formation of more chemically stable iron-silicate precipitates in the leachate. Iron has also been shown to mitigate the beneficial effect of bentonite backfill.

- Quench Effects

  Most wasteform durability experiments are conducted at elevated temperatures under hydrothermal conditions. The experimental set-ups require that the leaching vessel be brought to ambient temperature and pressure for analyses to avoid loss of leachate. During this temperature reduction (quench), some dissolved species which are saturated at higher temperature may precipitate out of the solution. In most such elevated-temperature experiments, knowledge of the composition of leachates at the test (higher) temperature is desirable for predicting performance in a repository. Therefore, it is essential to design experimental set-ups which would allow the sampling of the leachate at the temperature at which the test is conducted.

- Colloid and Precipitate Formation

  Aqueous colloid formation in leachates which generally include both actinides and silica, if significant, could provide a mechanism for radionuclide transport not predicted by silica solubility limited models. The size, stability, and composition of such colloids need to be evaluated along with the fraction of total inventory in colloidal and precipitate form. Formation of pseudo-colloids [actinides released from the glass into the leachate attaching themselves on to the colloids released from the waste container material (e.g., iron and aluminum)] and their precipitation characteristics/kinetics need also to be understood in more detail than in the present knowledge base to enable inclusion of the effects of colloids and precipitates in advanced performance assessment models.

- Secondary Mineral Formation (Surface Layers)

  Most wasteform tests under unsaturated or very low aqueous flow conditions lead to the formation of reaction products which are, in most cases, crystalline but could also be amorphous. Solubility calculations and geochemical codes are used to predict equilibrium concentrations of such products. This approach would be valid provided the reaction products are known, the reaction path is understood, and the minerals formed are equilibrium phases. Such is not the current state of understanding. A number of minerals formed on the glass wasteform are probably metastable. Methods of evaluating wasteform degradation reaction paths, therefore, require further development. It is also necessary to expand the thermodynamic properties database of the secondary minerals that have been observed on HLW borosilicate glasses, especially at extremely high SA/V ratios which are considered more representative of an unsaturated repository environment.

- Radiation Effects

  Although the measurable effects of α-decay on wasteform properties are minimal at room temperature, the behavior at elevated temperatures and at longer exposure times remains unpredictable due to insufficient data. It is recognized that the effects of radiation at elevated temperatures may be decreased due to increased thermal recovery; however, higher temperatures may result in other microstructural changes or defects that are not predictable based on ambient temperature data. Therefore, studies of radiation-induced changes in microstructure need to be conducted at elevated temperatures up to ~350°C, as such a range of temperatures are possible according to current repository preliminary designs.

- Amorphization of Devitrified Phases Due to Radiation

  In crystalline phases, the radiation-induced transformation to amorphous phases has the greatest potential for detrimental effects. Large volume changes may induce microcracking. The long-term effect of amorphization on leaching rate needs further experimental investigation.

- Use of Natural Analogs for Validating Models and Use of Glasses of Great-Age for Laboratory Leaching Tests

  Regulations pertaining to the management of HLW in the United States require that the performance of the geological repository be estimated for a period of 10,000 years. Since experiments cannot be conducted for such long periods of time, the predictive performance models and codes have to be validated in some other way. Use of natural analogs of borosilicate glasses is suggested as an option which needs more attention. Glasses of great-age (if relevant to HLW borosilicate glasses) should be included along with borosilicate wasteforms in laboratory leaching studies. Very few studies have been performed on natural glasses under relevant repository environments.

- Initiation of Long/Very-Long Term Leaching Tests

  One of the most critical aspects of the performance evaluation of borosilicate glasses is the extrapolation of their degradation behavior (as determined in short-term experiments) to long periods of time. The current trend is to develop shorter duration tests as opposed to longer term tests; this trend needs to be reversed, or additional standard long-term tests need to be developed that will provide model validation data over the next 20 years and will also allow the sample exposure to be extended to an additional 50 years or more (total of 70 years or more) to provide confirmation test data. Such long-term controlled experiments need to be initiated immediately.

- Fully Radioactive Versus Simulated HLW Test Samples

  There is evidence that fully radioactive glasses may release some radionuclides through the mechanism of colloid formation and that such a phenomenon cannot be simulated in wasteforms with surrogates of the radionuclides. Via this release mechanism, the concentration of selected radionuclides can exceed the solubility limit of the groundwater. Therefore, at least a few radioactive specimens (control samples) should be included in most testing protocols. The information generated on colloid formation in glasses containing radioactive wastes would be essential for calculating radionuclide transport in the far-field of the repository. Increased numbers of tests on radioactive glasses are recommended.

- Development of a Standardized Very High SA/V (Steam) Leaching Test

  Most chemical durability tests are conducted at very low SA/V ratios (i.e., the specimens are fully submerged in a large quantity of water). This condition does not simulate the unsaturated repository condition. The repository condition would be better simulated by steam or a low-moisture air environment. Standard testing procedures like those for saturated phase leaching (MCC-1 or PCT) should be developed to allow comparison of data generated under unsaturated environmental conditions from different laboratories. Data from experiments conducted under very high SA/V conditions followed by aqueous leaching tests (i.e., leaching of aged specimens) would provide information related to the protective nature of surface alteration phases formed on the glass. Currently, such information, particularly incorporating the influence of waste package corrosion products, is unavailable.

- Liquid-Liquid Phase Separation

  Understanding of the wasteform chemical composition bounds leading to liquid-liquid phase separation should be a high-priority concern, as the phenomena may have considerable effect on the long-term performance of the final product. Examples are available which show full-size glass monoliths with poor performance due to liquid-liquid phase separation (formation of silica-rich phase and SiO_2 polymorphs crystals upon cooling below the glass transition temperature) resulting from small deviations in the composition of the melt.

- Tests Under More Than One SA/V Ratio Test Condition

  Data should be generated under at least three distinct and widely different SA/V ratios [i.e., very low (MCC-1 type), medium (PCT type), and very high (steam test)] to better understand the response of the wasteform under likely variable condition during the 10,000 years when its performance has to meet federal regulations. In addition, tests should be performed under high-flow conditions to determine the intrinsic (congruent dissolution) properties of the wasteform. Understanding of the surface layer formation is essential for the proper interpretation of flowing leachant experiments. An overwhelming majority of the leaching experiments are currently being conducted only under PCT conditions. The information that can be obtained from such test conditions does not provide complete understanding of the borosilicate HLW glass necessary for modeling long-term performance.

- Open-System Experiments

  Since the repository is an open-system, leaching experiments should be designed which would allow the ingress of air during the period when leachant (water) is in contact with air for determining the wasteforms chemical durability. Currently, a majority of the tests are being conducted in a closed-system set-up. Such tests do not adequantely represent the repository environment that will be experienced by the wasteform.

- Influence of Microbial Activity on Wasteform Degradation

Microbes are known to have significant influence on the degradation of metallic materials through the formation of metabolic products. Therefore, such activities can be expected to affect waste-package component degradation, leading to possible secondary affects on the glass wasteform degradation. This subject is of considerable interest as the repository is expected to be open for a period of approximately 70 years prior to the permanent closure, which may provide an opportunity for the introduction of microbes that do not exist in the geological formation. Currently, no information is available on the possible effects of microbial activity on the borosilicate glass wasteforms.

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