United States Department of Energy

Office of Waste Management

HIGH-LEVEL WASTE BOROSILICATE GLASS A COMPENDIUM OF CORROSION CHARACTERISTICS VOLUME 1

U. S. Department of Energy
Office of Waste Management
Office of Eastern Waste Management Operations
High-Level Waste Division

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MASTER

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**HIGH-LEVEL WASTE BOROSILICATE GLASS:
A COMPENDIUM OF CORROSION CHARACTERISTICS,
VOLUME I**

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PREFACE

Current plans for the management of high-level nuclear waste stored in tanks in the United States involve converting the waste into a canistered borosilicate glass form "acceptable for disposal" in a deep mined geologic repository [FYP-1991]. After a period of interim storage, the intent is that this canistered borosilicate glass waste will be transported to a geological repository location and packaged for final disposal.

The process through which the canistered borosilicate glass waste produced by the vitrification facilities will be established as "acceptable for disposal" is likely to be complex because of the many interested parties involved. The first phase in this process involves the period prior to start up of the vitrification facilities. Because it was recognized that this first phase was likely to considerably predate licensing of a geologic repository, the DOE instituted a Waste Acceptance Process (WAP) which identifies information, criteria, and documentation requirements for waste form and process startup acceptance [CHACEY-1990]. This three-volume set of documents (referred to as the "Compendium" for short) is intended to complement the WAP documentation. It addresses the chemical durability of borosilicate glass waste forms, under the range of reasonably credible conditions to which they might be exposed in service, by consolidating available information on the current understanding of waste glass alteration. It does not, however, include comparisons of waste glass chemical durability with any objective or subjective standards that interested parties may use in making the judgment that the borosilicate glass waste forms are "acceptable for disposal."

The Compendium has been subjected to an extensive independent technical review by an expert panel designated as the Technical Review Group (TRG). The TRG was chaired by Dr. David E. Clark of the University of Florida (USA). Other members of the TRG were Dr. Robert H. Doremus of Rensselaer Polytechnic Institute (USA), Dr. Bernd E. Grambow of Kernforschungszentrum Karlsruhe (Germany), Dr. J. Angwin Marples of the Atomic Energy Authority (UK), and Dr. John M. Matuszek of JMM Consultanting (USA). The results of this review are documented in a separate report entitled "Waste Glass Compendium Technical Review Group Review Comment Report."

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GLOSSARY (Contd.)

exfoliation:	for this document, "exfoliation" involves the separation of a portion of the surface alteration layer from the underlying glass substrate; synonymous with spallation
forward rate:	also referred to as the "initial rate"; designates the rate of glass corrosion that is observed initially upon immersion in the leachant. It corresponds to the rate observed when the dissolution affinity term in the glass corrosion rate models has its maximum value (i.e., when the leachate has its minimum feedback effect on inhibiting the rate of corrosion) (see Fig. 1-2, Volume I)
gel layer:	the term used to define the layer(s) where the glass structure is highly hydrolyzed
glass dissolution:	a general term referring to the release of glass components into solution
glass reactivity:	the tendency of glass to undergo corrosion, weathering, or leaching
glass transition temperature:	the temperature at which glass, on cooling, transforms from a viscoelastic to an elastic material characterized by the onset of a rapid change in thermal expansivity
hydration:	in the context of this document, "hydration" is used to refer to the set of processes involved in network hydrolysis and transport of the species involved
hydration aging:	synonymous with weathering
in situ:	in place
intermediate elements:	elements that can serve as network forming or network modifying elements
leachability:	a general term referring to selective dissolution of elements in glass
leachant:	solution used for leaching or corrosion tests
leachate:	solution obtained by leaching or corrosion of glass
leaching:	selective removal of elements as a result of interaction with aqueous solutions

GLOSSARY

affinity (of reaction):	synonymous with "reaction potential"; denotes the rate of change of the Gibbs free energy with respect to the extent of reaction progress
alpha recoil nucleus:	energetic daughter isotope produced in alpha decay; the energy of the daughter nucleus results from recoil associated with conservation of momentum in the decay process
alteration:	any physical or chemical change
bridging oxygen:	oxygen atoms whose two covalent bonds are used to form a network structure
canistered waste form:	waste form in a sealed canister
colloids:	colloids are small particles whose properties in solution are dominated by the solution/particle interfacial region. Typically they range in size from about 1 nm to 1 μ m
condensation reactions:	reverse network hydrolysis reactions; bridging oxygen bonds are formed
corrosion:	the alteration of glass caused by reaction with chemicals (including water and water vapor) which starts at the glass surface
critical fracture toughness:	a material property used to determine the ease with which a flaw grows in the material under torsion, impact, fatigue, or other loading conditions; a high fracture toughness indicates that it is difficult to make a crack propagate through the material
dealkalization:	leaching of alkali metals; involves ion exchange or hydrolysis reactions at non-bridging oxygen sites and diffusion of reacting species
devitrification:	the conversion of vitreous or glass material into a nonvitreous (e.g., crystalline) material
diffusion layer:	alkali-depleted layer immediately adjacent to the fresh glass surface
durability:	inverse of glass reactivity; relative term to describe a glass' resistance to alteration

GLOSSARY (Contd.)

liquidus temperature:	the temperature at which observable crystals appear upon cooling (or disappear upon heating) of glass
network dissolution:	solvation of network-forming elements; special case of the network hydrolysis reaction wherein the hydrolyzed fragments are dissolved in the contacting solution
network-forming elements:	elements that are bonded to bridging oxygen atoms in the glass
network hydrolysis:	chemical reaction in which bridging oxygen bonds are broken resulting in break up of the glass network
network-modifying elements:	elements in the glass that are attached to the framework by nonbridging oxygen atoms
nonbridging oxygen:	oxygen atoms for which one of the bonds is not utilized to form the network (e.g., ionic bonding)
pitting:	localized corrosion
polymerization:	synonymous with condensation in this context; a chemical reaction in which a large number of relatively simple molecules combine to form chain-like macromolecules
precipitated layer:	a layer formed by precipitation of amorphous or crystalline material from bulk solution
precipitation:	process that results in formation of new solid phases (minerals, etc.) from dissolved constituents in solution
process:	in the context of this document, a "process" is a sequence of reaction and mass transport steps that convert a system from an initial to a final state. Sequential processes are processes for which the final state of the first process is the initial state of the succeeding process. Parallel processes are different sequences of reaction and transport steps that transform a system from the same initial to some final state(s)
reaction zone:	synonymous with diffusion layer; refers to the layer of partially altered glass immediately adjacent to the pristine glass. The glass in the reaction zone is altered principally by ion exchange, some network hydrolysis, and interdiffusion of reactants (e.g., H_3O^+) and leachable components (e.g., alkali metals and boron)

GLOSSARY (Contd.)

release:	<p>in the context of this document, "release" refers to the conversion of waste glass components (include radionuclides), originally immobilized in the glass matrix, into a form (generally solute and/or colloidal) which can move by diffusive, advective, or dispersive processes in a fluid that contacts the waste glass (e.g., region 4 of Fig. 1-3 in Volume I). Radionuclides associated with (i.e., incorporated into or adsorbed onto) a fixed or immobile substrate are generally not considered to be "released". In contrast to use of "release" in regulatory documents, its usage in this document does not connote movement or transport of radionuclides across any spatial boundary</p>
redox state:	<p>general term referring to the reducing-oxidizing state of a medium</p>
saturation rate:	<p>also referred to as the "long-term rate"; designates the rate of glass corrosion that is approached asymptotically in static leach testing. It corresponds to the rate observed when the dissolution affinity term in glass corrosion rate models approaches zero (i.e., when the leachate has its maximum feedback effect on inhibiting the rate of corrosion) (see Fig. 1-2, Volume I)</p>
secondary phases:	<p>solid materials produced by glass alteration</p>
spallation:	<p>breakoff, exfoliation, or detachment of surface layers from the glass substrate</p>
speciation:	<p>refers to the molecular and ionic forms of elements dissolved in aqueous solutions</p>
steady state:	<p>a condition of a dynamic system wherein one or more of the system variables does not change with time (i.e., has a time derivative equal to zero)</p>
Stern layer:	<p>a layer adjacent to the surface of a charged particle in solution which extends outward to the centers of the closest counter ions. In the Stern layer, the electric potential drops linearly with distance from the particle surface, while beyond the Stern layer it drops exponentially in the Gouy atmosphere of counter ions</p>

GLOSSARY (Contd.)

surface area:	in this document, "surface area" refers to the total area of the glass surface that may be contacted by water; it includes the surfaces that define cracks which are connected to the external surface. In the ratio S/V , the surface area represents the amount of glass available to react and the solution volume represents the volume available to dilute the reaction products
surface layers:	the assemblage of corrosion products formed on the glass surface
transition state theory:	a theoretical method for calculating reaction rates based on a statistical mechanical calculation of the thermodynamic properties of the potential energy surface separating the reactants and products of a chemical reaction
validation:	the process of ensuring that a model accurately simulates the behavior of the system that is modeled
verification:	the process of ensuring that a model or computer code does execute the intended operations
waste form:	borosilicate glass containing high-level waste
weathering:	glass corrosion due to intermittent water, humid air (with or without reactive gases such as carbon dioxide and sulfur dioxide), and/or water vapor contact
zeta potential:	the electric potential at the interface between the bulk liquid and the envelope of water that surrounds, and moves with, a particle

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LIST OF ACRONYMS

ABS	<u>A</u> lkali <u>B</u> orosilicate (Glass)
AES	<u>A</u> uger <u>E</u> lectron <u>S</u> pectroscopy
ANL	<u>A</u> rgonne <u>N</u> ational <u>L</u> aboratory
ASTM	<u>A</u> merican <u>S</u> ociety for <u>T</u> esting and <u>M</u> aterials
AVH	<u>A</u> telier <u>V</u> itrification <u>L</u> a <u>H</u> ague
AVM	<u>A</u> telier <u>V</u> itrification <u>M</u> arcoule
BDAT	<u>B</u> est <u>D</u> emonstrated <u>A</u> vailable <u>T</u> echnology
CC	<u>C</u> omplexant <u>C</u> oncentrate
CFR	<u>C</u> ode of <u>F</u> ederal <u>R</u> egulations
CVS	<u>C</u> omposition <u>V</u> ariability <u>S</u> tudy
DIW	<u>D</u> eionized <u>W</u> ater
DOE	<u>U</u> . <u>S</u> . <u>D</u> epartment of <u>E</u> nergy
DWPF	<u>D</u> efense <u>W</u> aste <u>P</u> rocessing <u>F</u> acility
EA	<u>E</u> nvironmental <u>A</u> ssessment
EBS	<u>E</u> ngineered <u>B</u> arrier <u>S</u> ystem
EDS	<u>E</u> nergy <u>D</u> ispersive <u>X</u> - <u>R</u> ay <u>S</u> pectroscopy
EELS	<u>E</u> lectron <u>E</u> nergy <u>L</u> oss <u>S</u> pectrometer
EMP	<u>E</u> lectron <u>M</u> icroprobe analysis (sometimes EMA <u>E</u> lectron <u>M</u> icroprobe <u>A</u> nalysis)
EPA	<u>U</u> . <u>S</u> . <u>E</u> nvironmental <u>P</u> rotection <u>A</u> gency
ESCA	<u>E</u> lectron <u>S</u> pectroscopy for <u>C</u> hemical <u>A</u> nalysis
FEH	<u>F</u> ree <u>E</u> nergy of <u>H</u> ydration (Model)
FTIR	<u>F</u> ourier <u>T</u> ransform <u>I</u> nfrared
HLW	<u>H</u> igh- <u>L</u> evel <u>W</u> aste
HLLW	<u>H</u> igh- <u>L</u> evel <u>L</u> iquid <u>W</u> aste
HM	<u>H</u> igh <u>M</u> etal (aluminum)
HTGR	<u>H</u> igh- <u>T</u> emperature <u>G</u> as- <u>C</u> ooled <u>R</u> eactor
HWVP	<u>H</u> anford <u>W</u> aste <u>V</u> itrification <u>P</u> lant
IAEA	<u>I</u> nternational <u>A</u> tomc <u>E</u> nergy <u>A</u> gency
ICP	<u>I</u> nductively <u>C</u> oupled <u>P</u> lasma
IRRS	<u>I</u> nfrared <u>R</u> eflection <u>S</u> pectroscopy
ISO	<u>I</u> nternational <u>O</u> rganization for <u>S</u> tandardization
JVF	<u>J</u> apanese <u>V</u> itrification <u>F</u> acility
LFCM	<u>L</u> iquid- <u>F</u> ed <u>C</u> eramic- <u>L</u> ined <u>M</u> elter
MCC	<u>M</u> aterials <u>C</u> haracterization <u>C</u> enter
MFT	<u>M</u> elter <u>F</u> eed <u>T</u> ank
MIIT	<u>M</u> aterials <u>I</u> nterface <u>I</u> nteraction <u>T</u> ests
NBO	<u>N</u> onbridging <u>O</u> xygen
NCAW	<u>N</u> eutralized <u>C</u> urrent <u>A</u> cid <u>W</u> aste
NCRW	<u>N</u> eutralized <u>C</u> ladding <u>R</u> emoval <u>W</u> aste
NMR	<u>N</u> uclear <u>M</u> agnetic <u>R</u> esonance
NRC	<u>U</u> . <u>S</u> . <u>N</u> uclear <u>R</u> egulatory <u>C</u> ommission
PBB	<u>P</u> ermian <u>B</u> asin <u>B</u> rines
PCCS	<u>P</u> roduct <u>C</u> omposition <u>C</u> ontrol <u>S</u> ystem
PCT	<u>P</u> roduct <u>C</u> onsistency <u>T</u> est
PFF	<u>P</u> lutonium <u>F</u> inishing <u>P</u> lant

LIST OF ACRONYMS (Contd.)

PNL	<u>Pacific Northwest Laboratory</u>
RBS	<u>Rutherford Backscattering</u>
RNM	<u>Random Network Model</u>
RNRA	<u>Resonance Nuclear Reaction Analysis</u>
SAED	<u>Selected Area Electron Diffraction</u>
SBS	<u>Structural Bond Strength (Model)</u>
SEM	<u>Scanning Electron Microscopy</u>
SEM/EDS	<u>Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy</u>
SIMS	<u>Secondary Ion Mass Spectrometry</u>
SIPS	<u>Secondary Ion Photon Spectroscopy</u>
SME	<u>Slurry Mix Evaporator</u>
SRL	<u>Savannah River Laboratory</u>
SRS	<u>Savannah River Site</u>
S/V	<u>Surface-Area-to-Solution-Volume (Ratio)</u>
TEM	<u>Transmission Electron Microscopy</u>
TVF	<u>Tokai (Japan) Vitrification Facility</u>
WAPS	<u>Waste Acceptance Product Specifications</u>
WDS	<u>Wavelength Dispersive X-Ray Spectroscopy</u>
WIPP	<u>Waste Isolation Pilot Plant</u>
WSRC	<u>Westinghouse Savannah River Company</u>
WV	<u>West Valley</u>
WVDP	<u>West Valley Demonstration Project</u>
XPS	<u>X-Ray Photoemission Spectroscopy</u>
XRD	<u>X-Ray Diffraction</u>

EXECUTIVE SUMMARY

The objective of this document is to summarize scientific information pertinent to evaluating the extent to which high-level waste borosilicate glass corrosion and the associated radionuclide release processes are understood for the range of environmental conditions to which waste glass may be exposed in service. Alteration processes occurring within the bulk of the glass (e.g., devitrification and radiation-induced changes) are discussed insofar as they affect glass corrosion.

This document is organized into three volumes. Volumes I and II represent a tiered set of information intended for somewhat different audiences. Volume I is intended to provide an overview of waste glass corrosion, and Volume II is intended to provide additional experimental details on experimental factors that influence waste glass corrosion. Volume III contains a bibliography of glass corrosion studies, including studies that are not cited in Volumes I and II. Volume I is intended for managers, decision makers, and modelers; the combined set of Volumes I, II, and III is intended for scientists and engineers working in the field of high-level waste.

Important points from the contents of Volumes I and II are summarized as follows:

Volume I

- Borosilicate glass was selected in 1982 as the reference waste matrix for solidifying high-level radioactive wastes (HLW) stored in tanks at Savannah River and West Valley following an extensive evaluation of alternative waste form materials (Section 1.3).
- Most countries throughout the world that have HLW from the reprocessing of nuclear fuel have selected or are evaluating borosilicate glass as a final waste form (Section 1.4).
- The corrosion rate of waste glass depends on the glass characteristics and the environmental conditions to which it may be exposed in service. Although neither the waste glass characteristics nor the environmental service conditions can yet be precisely defined, the plausible waste glass characteristics and service conditions are presented to orient the reader concerning the relevant testing and modeling conditions (Section 2).
- The corrosion of waste glass results from ion exchange and glass network hydrolysis and dissolution reactions that occur at the interface between the glass and contacting water solutions. Although all of these reactions occur simultaneously, their relative rates change as the glass corrosion progresses. It is useful to identify three stages in the corrosion of waste glass. The first two stages, which occur in experimentally accessible times, are well understood. The first stage corresponds to an initial transient period when ion exchange is dominant. Because this represents a short period (usually lasting a few days at most) it is important primarily because of its effects on the leachate pH. The second stage, which spans the duration of most laboratory tests, is characterized by hydrolysis and dissolution of the glass network. The rate of corrosion during this stage is usually controlled by the dissolution step although there is evidence that, under some circumstances, mass transport (i.e.,

diffusion) through the alteration layers on the glass surface may control the rate. Although the experimentally determined rates for stage 2 vary considerably depending on the glass composition and test conditions, the characteristic "saturation rates" for well-formulated borosilicate glass indicate that borosilicate glass may be an effective barrier for radionuclide release. However, definitive statements on performance must be based on performance assessment calculations. The third stage corresponds to times beyond the experimentally accessible times for laboratory testing. Although glass corrosion during this third stage is believed to involve the same reactions as those discussed above for stages 1 and 2, the record of evidence for the dominant reactions is comparatively sparse. The relative importance of ion exchange, network hydrolysis, and dissolution contributions to long-term corrosion is not established (Section 1.2).

- Current models for the rate of waste glass corrosion are based on utilization of transition state theory to describe the rate of the dissolution reaction, which most of the experimental evidence suggests is rate determining during stage two. Because the rate of dissolution depends on the dissolution affinity, reaction path models are used to evaluate the dissolution affinity as a function of reaction progress. Some models also include diffusion terms to accommodate reaction conditions where the rate of mass transport through surface alteration layers can be rate limiting. The current models are generally successful in reproducing qualitative and even quantitative features of the experimentally observed waste glass corrosion behavior. In particular, they explain effects (e.g., the time dependence of the corrosion rate, S/V effects, and leachate flow rate effects) that are associated with changes in the leachate chemistry (e.g., the silicic acid concentration) as corrosion progresses. However, they have been less successful in predicting the effects of waste glass composition on the corrosion rate (Section 3.3).
- Estimates of the long-term waste glass corrosion and weathering rates must rely on modeling predictions. Implementation of mechanistically based glass corrosion models for repository performance assessment has been limited. Utilization of the current models for extrapolations into stage three must be tempered by the realization that the processes responsible for controlling the long-term corrosion rate (when the leachate is saturated with silicic acid and other glass dissolution components) have not been positively identified. Two processes have been suggested. The first involves continued dissolution of the matrix as long-term nucleation and precipitation of secondary phases remove silicic acid and other glass corrosion products from solution. The second involves a return to corrosion dominated by ion-exchange when the residual dissolution affinity becomes very small. For this process, the rate of ion-exchange may be determined by the rate of water diffusion through the reaction zone (Sections 3.1, 3.2, and 3.3).
- There are many sources of the remaining uncertainties in waste glass corrosion and the associated radionuclide release rates. These vary from uncertainties in the experimental data base (e.g., comparatively sparse data base for weathering conditions) to uncertainties associated with extrapolation into the distant future. The importance of reducing these uncertainties will depend on the performance allocated to the glass (Section 4).

- Based on the empirically determined corrosion rates and radionuclide retention factors it appears that, while properly formulated borosilicate glass can be an effective barrier for radionuclide release, it is important to consider its long-term corrosion performance in composition formulation and in design of the geologic repository (Section 4).

Volume II

- The surface alteration layers are usually non-protective (i.e., they do not influence the rate of corrosion by inhibiting mass transport to or from the corroding glass surface). However, under some conditions (e.g., in leachants containing magnesium ions and in very alkaline solutions) the surface layers have been observed to act as mass transport barriers and thereby influence the rate of corrosion. The principal effects, under most conditions, appear to be through the effects of the surface layer phase assemblage on the leachate composition (e.g., silicic acid concentration). The leachate composition influences the corrosion rate through a feedback effect on the glass matrix dissolution rate (Section 2.1).
- The effects of glass composition on the corrosion rate are complex. Although there are a lot of experimental data and modeling approaches for correlating short-term durabilities, the experimental evidence for the effects of composition on the longer term corrosion rates is limited. As illustrated by varying the Al content, the effects of composition may be different for short-term and long-term tests; Al increases the durability as measured by short-term tests while, under some conditions, it may reduce durability as measured in long-term tests (Section 2.2).
- The observed effects of flow rate and surface-area-to-solution-volume ratio can be interpreted in terms of the effects of these parameters on the silicic acid concentration and pH of the leachate. High surface-area-to-volume tests are useful in accelerating reaction progress. The "forward reaction" and "saturation rates" for a number of borosilicate glasses are presented. These rates depend on the glass composition and test conditions (Section 2.3).
- The effects of temperature can be correlated using the Arrhenius equation. Nonlinearities in the Arrhenius plots and the wide range of activation energies are probably due to changes in the rate-determining steps in the corrosion process due to factors such as reaction time, evolving solution chemistry, and temperature (Section 2.4).
- The principal effect of radioactive decay appears to be the effect of radiolysis of the glass corrosion environment; radiation damage effects appear to be less important due to damage annealing. The radiolysis effects may increase or decrease the corrosion rate depending on the glass composition and environmental conditions involved (Section 2.5).
- Microbes may influence waste glass corrosion through their effects on the local environments at the corroding glass surface. Relatively little information is available to evaluate the importance of these effects (Section 2.6).

- A large fraction of released radionuclides may become immobilized upon incorporation into or sorption onto mineral phases generated by corrosion of the glass and other repository materials. The alteration layers formed on the glass typically account for the retention of about 90% of neptunium, 97% of plutonium, and 99% of americium as the glass corrodes (Section 2.7).
- Sorption of radionuclides onto colloids present in the groundwater and those generated during glass corrosion will strongly affect the distribution of actinides between mobile and stationary phases. Sorption onto colloids may cause the mobile concentrations of radionuclides to exceed the dissolved concentrations. Sorption is specific to the host mineral phase and the oxidation state of the radionuclide. Sorption of nuclides in tri- and tetravalent oxidation states is usually stronger than that of the penta- and hexavalent states (Section 2.7).
- The weathering of waste glass can be interpreted in terms of the same underlying corrosion processes as those observed for aqueous corrosion. In fact, it is instructive to consider weathering as a high S/V aqueous corrosion condition (Section 3).
- The results obtained from field testing of waste glass corrosion in a variety of underground environments are generally consistent with the results obtained in laboratory tests (Section 4).
- The rate of waste glass corrosion is known to be influenced by interactions with other materials that may be utilized in an underground repository. Specifically, materials that can be incorporated into the surface alteration layers or cause silicic acid to be removed from the leachate by precipitation can influence the corrosion rate. For example, incorporation of lead into the surface layers can decrease the corrosion rate while iron, aluminum, and bentonite clay can increase the rate of corrosion by promoting the precipitation of silicate phases (Section 4).
- Examination of natural glasses, particularly basaltic glasses, has provided evidence that the long-term corrosion processes for naturally altered glasses are similar to those observed in laboratory studies of waste glasses; this provides important evidence that models, based on processes that are important in laboratory tests, can be used for long-term extrapolation (Section 5).

HIGH-LEVEL WASTE BOROSILICATE GLASS: A COMPENDIUM OF CORROSION CHARACTERISTICS, VOLUME I

1.0 INTRODUCTION

Current plans call for the United States Department of Energy (DOE) to start up facilities for vitrification of high-level radioactive waste (HLW) stored in tanks at the Savannah River Site, Aiken, South Carolina, in 1995; West Valley Demonstration Project, West Valley, New York, in 1996; and at the Hanford Site, Richland, Washington, after the year 2000. The product from these facilities will be canistered HLW borosilicate glass, which will be stored, transported, and eventually disposed of in a geologic repository. The behavior of this glass waste product, under the range of likely service conditions, is the subject of considerable scientific and public interest. Over the past few decades, a large body of scientific information on borosilicate waste glass has been generated worldwide. The intent of this document is to consolidate information pertaining to our current understanding of waste glass corrosion behavior and radionuclide release.

The objective, scope, and organization of the document are discussed in Section 1.1, and an overview of borosilicate glass corrosion is provided in Section 1.2. The history of glass as a waste form and the international experience with waste glass are summarized in Sections 1.3 and 1.4, respectively.

1.1 Objective, Scope, and Organization

1.1.1 Objective

The objective of this document is to summarize scientific information on waste glass corrosion processes for the environmental conditions to which high-level waste glass may be exposed in service. This information is useful for evaluating the extent to which waste glass corrosion and the associated radionuclide releases are understood. It should also be useful in considering the qualitative and quantitative effects of waste glass on the near-field chemistry and on performance assessment source terms in a geologic repository.

The specific waste glass corrosion characteristics addressed in this document are:

- Waste glass corrosion and weathering rates due to groundwater and/or water vapor contact and
- rates and forms (solutes and colloids) in which radionuclides are released from corroding waste glass into contacting water.

Waste glass corrosion and weathering rates are the primary characteristics addressed; radionuclide release rates and forms are a secondary focus.

1.1.2 Scope

The study of waste glass corrosion over the past few decades has been motivated primarily by interest in determining radionuclide release rates from waste glass following geologic disposal. However, radionuclide release rates are only partially determined by the waste form. In fact, radionuclide release rates from waste in a geologic repository have been estimated without consideration of waste glass corrosion characteristics—for example, on the basis of radioelement solubilities and "external field" (see Fig. 1-3) mass transport rate limitations [PIGFORD-1985]. The scope of this document is limited to consideration of (1) glass/environment interactions and other processes occurring in the immediate vicinity of the glass (e.g., glass corrosion; glass weathering; redox; hydrolysis and complexation reactions in solution; radionuclide sorption and coprecipitation with secondary phases) that may influence radionuclide release rates and (2) bulk waste glass alteration processes (e.g., cracking, phase transformations/devitrification, and radiation damage) that may influence corrosion and weathering rates and/or radionuclide release rates.

Because of the long half-lives of some radionuclides (see Section 2.1.2.3), waste glass corrosion processes and associated radionuclide releases may have to be predicted for very long time periods (extending to tens of thousands of years after emplacement in a repository). Credible long-term predictions should be based on a sound understanding of the processes involved. A suitable approach for developing credible long-term predictive models involves identification of the corrosion processes, development of a sound understanding of these processes through iterative experimental and modeling steps, and model validation [ASTM-1991]. The intent of this document is, therefore, to summarize the current understanding of waste glass corrosion and associated radionuclide release processes using information from worldwide sources. Sources were selected for illustrative purposes and should not be interpreted as a complete set of pertinent references. Information, opinions, and interpretations that are not attributed to other sources should be assumed to be those of the authors of this document. The types of scientific information discussed include experimental testing data, data from natural and historical synthetic glasses, interpretations of data in terms of mechanistic understanding of the underlying physical and chemical processes involved, and mechanistic predictive modeling. The scope also includes summary descriptions of waste glass products and of plausible conditions to which the glass products may be exposed during handling, storage, transportation, and eventual geologic disposal.

1.1.3 Organization

This document is organized into three volumes. Volumes I and II represent a tiered set of information intended for somewhat different audiences. Volume I is intended to provide an overview of waste glass corrosion, and Volume II is intended to provide additional experimental details on factors that influence waste glass corrosion. Volume III contains a bibliography of glass corrosion studies, including studies that are not cited in Volumes I and II. Volume I is intended for managers, decision makers, and modelers; the combined set of Volumes I, II, and III is intended for scientists and engineers working in the field of high-level waste disposal.

1.2 Overview of Borosilicate Waste Glass Corrosion

The following overview of borosilicate waste glass corrosion is included to provide an orientation or "frame of reference" for the subsequent more detailed discussion. It should also clarify constraints regarding the scope of the content.

1.2.1 Glass Corrosion Reactions

Silicate glasses are metastable and therefore do not reach thermodynamic equilibrium with aqueous environments. However, they are chemically durable because of the slow kinetics of both the corrosion reactions and of the transformations into more stable mineral phase assemblages. Recently, understanding of the kinetics of glass corrosion processes in aqueous solutions has improved significantly [CLARK-1979, -1992; LUTZE-1988b]. Glass corrosion begins when glass, at the interface with aqueous solutions, undergoes ion exchange and a number of network hydrolysis reactions; these reactions are summarized in Table 1-1. Reactions 2 and 3 are probably equivalent under most conditions because of the rapid hydrolysis of Na_2O to form NaOH . When water ionization is considered, reactions 1 to 3 are equivalent because the net effect is ion exchange. Likewise, reactions 4 and 5 and reactions 6 and 7 in Table 1-1 are equivalent. Hence, the aqueous corrosion of glass involves ion-exchange, network-hydrolysis, and network-dissolution reactions. Because ionization and dissolution are negligible in dry water vapor, corrosion in the dry vapor phase involves H_2O as the active corroding agent (see reactions 2 and 5).

Table 1-1. Glass Corrosion Reactions

	Reaction	Nomenclature
1	$\equiv\text{Si-O-Na} + \text{H}_3\text{O}^+ \rightleftharpoons \equiv\text{Si-OH} + \text{Na}^+ + \text{H}_2\text{O}$	Ion exchange
2	$2(\equiv\text{Si-O-Na}) + \text{H}_2\text{O} \rightleftharpoons 2(\equiv\text{Si-OH}) + \text{Na}_2\text{O}$	Hydrolysis reactions at nonbridging oxygen sites
3	$\equiv\text{Si-O-Na} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{Si-OH} + \text{Na}^+ + \text{OH}^-$	
4	$\equiv\text{Si-O-Si}\equiv + \text{OH}^- \rightleftharpoons \equiv\text{SiOH} + \equiv\text{Si-O}^-$	Network hydrolysis (forward reaction)
5	$\equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O} \rightleftharpoons \equiv\text{SiOH} + \equiv\text{Si-OH}$	Condensation (reverse reaction)
6	$\begin{array}{c} \text{OH} \\ \\ \equiv\text{Si-O-Si-OH} + \text{OH}^- \rightleftharpoons \equiv\text{Si-O}^- + (\text{H}_4\text{SiO}_4)_{\text{aq}} \\ \\ \text{OH} \end{array}$	Network dissolution (forward reaction)
7	$\begin{array}{c} \text{OH} \\ \\ \equiv\text{Si-O-Si-OH} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{Si-OH} + (\text{H}_4\text{SiO}_4)_{\text{aq}} \\ \\ \text{OH} \end{array}$	Condensation (reverse reaction)

Note: Although the reactions are written explicitly for Si and Na, similar reactions occur for other network-forming and network-modifying elements.

Source: Adapted from [ABRAJANO-1989].

Following dissolution in aqueous solution, the glass network-forming and network-modifying elements undergo a complex sequence of solution reactions that result in nucleation and precipitation of secondary phases after the solution becomes saturated. Such saturation may occur locally near the corroding surface or in the bulk solution. Generally, the net effect of these reactions on the glass surfaces is schematically illustrated in Fig. 1-1. The surface layers represent progressive stages in the corrosion process. Nearest to the interface with the unaltered glass is a layer (referred to as the "diffusion layer" or "reaction zone") where water has diffused into the glass and the glass has been altered as a result of ion exchange and some network hydrolysis (as reflected by the release of boron), but the network remains largely intact. Dissolution and local precipitation of the partially hydrolyzed glass in the diffusion layer results in pseudomorphic replacement of the glass by a gel layer enriched in the less soluble glass components (this gel layer may eventually undergo in-situ alteration to more stable crystalline phases and result in surface layer structures that are more complex than those illustrated in Fig. 1-1). The outermost layer results from nucleation and precipitation of secondary phases following saturation of the solution. These secondary phases may contain elements from the leachant as well as those from the corroding glass. Factors that influence the thickness of these layers and their influence on the kinetics of waste glass corrosion are summarized in the next section and discussed in more detail in Volume II, Section 2.1.

1.2.2 Glass Corrosion Reaction Kinetics

A major focus of this document is the rate of waste glass corrosion, so a brief overview follows of some of the major concepts involved in understanding glass corrosion kinetics. Each of the reactions discussed in Section 1.2.1 include three sequential steps:

1. Transport of reactant to the reaction location.
2. Chemical reaction.
3. Transport of products away from the reaction location.

Combination of the transport steps with the corrosion reactions in Table 1-1 makes it apparent that glass corrosion can be considered to consist of several parallel and sequential processes, each of which consists of a sequential chain of reaction and transport steps (see the Glossary for definition of "process"). The various processes contribute to the overall corrosion rate on the basis that, for parallel processes, the fastest process determines the rate whereas the slowest reaction or transport step determines the rate of each sequential process [WHITE-1992]. An important corollary to this general rule is that although the faster processes may make it difficult to detect slower processes in glass corrosion tests, the latter will only contribute significantly when the overall corrosion rate is low. Much of the research on waste glass corrosion deals with identifying the operative corrosion processes, the rate-limiting (or rate-controlling) steps in these processes, and the coupling between the operative processes. In the following paragraphs, the operative processes are identified together with the rate-controlling step in each process. For example, "diffusion-controlled ion exchange and alkali extraction" means that the process involves ion exchange and alkali extraction and the rate of the process is controlled by diffusion.

The corrosion of alkali silicate glasses in aqueous solutions results from a combination of two processes [GRAMBOW-1992], viz.

- Diffusion-controlled ion exchange and extraction of alkali ions. This process causes the interface between the glass and the reaction zone to move inward as the corrosion proceeds. The diffusion resistance is provided by the reaction zone.

Fig. 1-1. Schematic of Surface Layers on Corroded Glass (adapted from [MENDEL-1984]). The photomicrograph shows the reacted layers on WVCN50 glass reacted for 10 days in saturated steam at 200°C (adapted from [EBERT-1991a]) (see Figure 2-2 in Volume II).

- Dissolution-controlled hydrolysis of the glass matrix. This process causes the interface between the gel and reaction zone to advance inward as corrosion progresses. Under some circumstances, the rate of the dissolution reaction is controlled by mass transport through the surface layers (see Volume II, Section 2.1 for a detailed discussion).

The first of these processes includes network-hydrolysis-controlled diffusion of water into the glass at the glass/water interface, ion exchange, and release of boron, while leaving much of the affected network near the glass surface intact. The second results in complete degradation of the glass network in the affected region near the glass surface due to the hydrolysis and dissolution reactions shown in Table 1-1. While these processes occur simultaneously, their relative importance changes with time. It is instructive to divide glass corrosion into three stages. Stage 1 is characterized by a period when the corrosion is dominated by the diffusion-controlled ion-exchange process. Stage 2 is characterized by the occurrence of ion exchange, network hydrolysis, and network dissolution, with the overall rate of corrosion being controlled by the dissolution step. Stage 3 represents the long-term corrosion beyond experimentally accessible time; the processes that control the corrosion rate during this stage are less well established.

Upon initial immersion in water, both diffusion-controlled alkali extraction and dissolution-controlled corrosion occur in parallel. Initially, the former process is dominant because it proceeds at a faster rate. Both processes slow with time, but diffusion-controlled ion exchange slows more because of the increasing thickness of the diffusion layer. When the rate of dissolution equals the rate of diffusion, a steady-state condition occurs wherein the diffusion layer retains a constant thickness. Thereafter, the rate of diffusion and the overall corrosion rate are controlled by dissolution because the dissolution rate now controls the thickness of the diffusion layer. However, some evidence indicates that when the dissolution step slows sufficiently, the diffusion-controlled alkali-extraction process may again become rate limiting (see Section 3.1 for discussion of glass corrosion processes).

For a more complete understanding of the general concepts discussed above, complicating factors must be considered--such as the coupling between processes and the interdependencies between various steps in each process. For example, although the rate of ion exchange depends on the rate of dissolution because of the effects of the latter on the diffusion layer thickness, the rate of dissolution is influenced by ion exchange because of the effect of ion exchange on pH. The interdependency of the steps in the dissolution process is illustrated by the effects of precipitation of iron and aluminosilicates on lowering the silicic acid concentration (see Volume II, Section 2.2) which, in turn, increases the dissolution rate.

The processes discussed above cause the corrosion rate of borosilicate glass to be a complex function of many glass composition and environmental factors. Identification of the important factors and understanding how they influence the corrosion rate is a subject addressed extensively throughout Volumes I and II of this document. However, a short review of the corrosion behavior is provided below by way of an introductory background for the more detailed information presented later.

Figure 1-2 illustrates some of the typical characteristics of the variation in glass corrosion as a function of time as measured in static tests. It illustrates features observed in the normalized release of boron (a measure of cumulative corrosion) and the corresponding corrosion rate curves. The time axis is divided into three parts to illustrate the three stages of glass corrosion. At a temperature of 90°C,

Fig. 1-2. Schematic Showing Qualitative Behavior of Glass Corrosion vs. Time

the observed short-term corrosion rates are about $1 \text{ g/m}^2/\text{d}$ upon initial immersion in water. After decreasing monotonically, the rates for SRL 202 and the French R7T7 glass reach a steady value of about $2.5 \times 10^{-3} \text{ g/m}^2/\text{d}$ at 90°C [GRAMBOW-1991b; STRACHAN-1990; EBERT-1993], see Volume II, Section 2.3.4.

This time-dependent behavior of the cumulative corrosion and corrosion rate curves has been explained and modeled as arising from changes in the leachate (e.g., increased silicic acid concentration) that are produced by the corroding glass which, in turn, have a feedback effect that reduces the rate during Stage 2 of the corrosion process (see Section 3.3). In general, the time dependence of the corrosion rate for a particular glass composition is attributed to a variety of feedback effects associated with the reaction progress, e.g., the effects of the increasing diffusion layer thickness on the rate of diffusion in Stage 1 and the effects of the increasing concentrations of silicic acid (and other glass constituents) during Stage 2 (see Section 3.3). Since the time dependence can be attributed to the effects of reaction progress, it is useful to consider the corrosion rate as a function of

a generalized reaction progress parameter as illustrated in Fig. 1-2. The notion here is that the corrosion rate should be considered to be a function of reaction progress; the time dependence is determined by variation of the reaction progress with time.

Figure 1-2 illustrates several qualitative features of the corrosion rate of borosilicate glass. The rate exhibits a generally decreasing trend with reaction progress. As discussed in Section 2.3.4 of Volume II, two characteristic rates (i.e., a forward reaction rate and a saturation rate) can be identified corresponding to infinite dilution and silicon saturation conditions, respectively. The discontinuity in the rate curve (change in the slope of the cumulative corrosion curve) illustrated by the dashed lines near the end of Stage 2 in Fig. 1-2 indicate that the decrease in the corrosion rate may not be monotonic for some glasses at very high values of the reaction progress parameter (see Volume II, Section 2.3.3). Such effects are attributed to nucleation and precipitation of secondary phases that establish a lower saturation concentration of silicic acid (or other solution species) and thereby increase the affinity for glass dissolution. The occurrence and importance of such effects probably depends on the glass composition.

1.2.3 Glass Corrosion in an Underground Repository

The corroding glass system in a repository can be illustrated schematically as shown in Fig. 1-3. In this system, the gap region (i.e., region 4), which defines the corroding glass environment, may be filled with (1) groundwater, (2) two-phase air/water vapor mixtures with the liquid phase present as water films and/or dripping water, or (3) dry air/water vapor mixtures. The fluid mixture depends on the near-field scenario (see Sections 2.2.2 and 2.2.3). In this system, the glass corrosion rate and radionuclide release rate may be influenced by interaction with the various engineered barrier materials and by the rate of "external field" mass transport into these materials and the surrounding rock. In fact, such external field mass transport steps may control the rate of radionuclide release into the surrounding host rock [PIGFORD-1985]. However, for programmatic reasons, the scope of this document is limited to discussing processes that occur within the boundary between regions 4 and 5 (i.e., to the left of the region 4/5 boundary shown schematically in Fig. 1-3). The discussion includes information on how radionuclide release to region 4 is influenced by glass corrosion, by the dissolution of individual radioelements, by incorporation of radionuclides into the surface layers, and by formation of colloidal material. Only processes that occur in the glass, the corroded glass, and its immediate vicinity are discussed; other processes (e.g., mass transport constraints on the rate of release of radionuclides and other constituents of the glass to the external field environment) are not included.

As already noted, the corrosion behavior of glass beyond experimentally accessible time can be considered to represent Stage 3 of the corrosion process. Examination of historical and very old natural glasses that are analogous to waste glasses provides evidence that the processes observed during Stages 1 and 2 are likely to control waste glass corrosion in Stage 3, although the specific process steps controlling the corrosion rate are not well established. Both experimental evidence and theoretical understanding suggest that the long-term rates are likely to be slower than those observed in short-term experiments, but several challenges remain in understanding the long-term corrosion process. These challenges include identifying the dominant long-term processes and understanding the effects that could cause the rates of the familiar processes to increase (e.g., coupling of precipitation to dissolution). The remaining uncertainties and the significance of these uncertainties are discussed in Section 4.0.

- ① Reaction Zone (note: Reactions 1 through 5 in Table 1-1 occur in this layer as does interdiffusion of the reactants and exchanged cations)
- ② Gel Layer
- ③ Precipitated Layer
- ④ Fluid-Filled Gap
- ⑤ External Field
- ⑥ Boundary of the Engineered Barrier System

Fig. 1-3. Schematic of HLW Borosilicate Glass Corrosion Following Geologic Disposal

1.2.4 Significance of Glass Corrosion and Radionuclide Release Rate Data

Application of waste glass corrosion and associated radionuclide release rate data to estimate the corresponding fractional alteration and radionuclide release rates per year for a full-size glass log is useful in judging the significance of the more detailed testing and modeling results presented later in both Volumes I and II of this document.

No regulatory standards apply directly to the corrosion rate or associated radionuclide release rate from waste glass. However, it is instructive to compare the allowed fractional release rates from the engineered barrier system (EBS) [NRC-1986] to the fraction of the canistered glass that would be expected to corrode, and the fraction of the inventory of individual radionuclides that might be released, should the glass be contacted by groundwater in a repository. It is important to recognize, however, that while showing that the annual fractional release from each individual canister is lower than the NRC allowed fractional release from the EBS (which includes the whole ensemble of waste packages in the repository) would, for most scenarios, be sufficient, it is not necessary for compliance with the controlled release rate performance objective. It is not necessary because other components of the EBS (e.g., the waste package containers) will contribute to controlling the release from the EBS [STRACHAN-1990]. On the other hand, it may not suffice if, for example, the breached waste glass packages were exposed to weathering conditions for a number of years and were subsequently contacted by groundwater.

The fraction (F) of the canistered waste that would corrode per year is given by:

$$F = \frac{RA}{W} \quad (1)$$

where R is the glass corrosion rate (g/m²/yr), W is the weight (g) of the glass in a canister, and A is the surface area (m²) of the glass exposed to water. Because radionuclides can only be released from properly formulated waste glass as a result of breakdown of the glass network due to corrosion, the fractional release of individual radionuclides cannot exceed the fraction of the glass corroded. As discussed in Section 2.7.2 of Volume II, the ratio of the cumulative corrosion (as measured by the normalized release of boron) to the cumulative release of individual radionuclides is given by the retention factor (RF)_i. Hence, the fraction of the individual radionuclides that would be expected to be released per year from a corroding glass log is given by:

$$f_i = \frac{F}{(RF)_i} = \frac{RA}{W(RF)_i} \quad (2)$$

For defense waste glass, W = 1.7 x 10⁶ g. A is uncertain; it could vary from less than the glass log cross-sectional area (i.e., 0.55 m²) for weathering conditions to about a factor of 20 greater than the geometric area of the glass log (i.e., 4.8 m²) for aqueous corrosion conditions. As discussed in Section 1.2.2, a reasonable point value estimate of (R) is 2.5 x 10⁻³ g/m²/d.

Based on the values of the Eq. 1 variables that are discussed above and assuming that all of the fracture surfaces are contacted by water, the fraction (F) of the canistered waste that would corrode per year under saturation conditions is given by:

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

Because the values of A (see Section 2.1.2.2.2) and R (see Volume II, Table 2-5) can vary above and below the values used in the above estimate, the fractional corrosion rate of $5.2 \times 10^{-5} \text{ yr}^{-1}$ should be used only as a benchmark for assessing the significance of laboratory data. A proper estimate would require application of models such as those discussed in Section 3 to estimate F for the actual projected conditions in a repository during Stage 3 of the glass corrosion process.

As shown in Eq. 2, the fractional release rate of individual radionuclides from a corroding glass log requires an estimate of the retention factor (RF). The experimentally measured retention factors for Np, Pu, and Am release from R7T7 glass [VERNAZ-1992] are plotted in Fig. 1-4. This figure illustrates the point that only a fraction (~10% for Np, ~3% for Pu, and ~0.3% for Am) of the sparingly soluble radionuclides associated with the corroded glass are released. Using Eq. 2 and the above estimates for (RF)_i, the fractional release rates (f_i) for Np, Pu, and Am are $5.2 \times 10^{-6} \text{ yr}^{-1}$, $1.6 \times 10^{-6} \text{ yr}^{-1}$, and $1.6 \times 10^{-7} \text{ yr}^{-1}$, respectively. Comparison of these estimates of the fractional releases with the allowed releases for the isotopes of these elements (see Table 2-8) suggests that waste glass would contribute very significantly to regulatory performance objectives for radionuclide release from the EBS if the corrosion rate and radionuclide retention factors during Stage 3 of the corrosion process are indeed comparable to the values used above.

Fig. 1-4.

Logarithm of the Retention Factors for Actinides Released from R7T7 Glass at 90°C (data from [VERNAZ-1992]): (○) U, (□) ²³⁷Np, (◇) ²³⁸Pu, (◆) ²³⁹Pu, and (▲) ²⁴¹Am.

1.3 History of Glass as a Waste Form

Glass has been recognized as a promising medium for the immobilization of HLW because of the commonly perceived chemical durability of silicate glasses and the capacity of glass to incorporate many different elements--a necessity for radioactive waste immobilization [WHITE-1955]. The possible glass durability over very long time periods is indicated by the survival of naturally occurring glasses for millions of years and synthetic glasses for thousands of years. The technology for glass fabrication also has a long history. Glass has been made and used since ancient times, and borosilicate glasses have been made and used since the early 1900s [BOYD-1984].

Laboratory development of potential glass compositions for incorporation of HLW began in Canada in the mid-1950s [WHITE-1955] and in the U.S. in the late 1950s [GOLDMAN-1958, WATSON-1958]. Both phosphate- and borosilicate-based glasses were initially investigated. However, because of the corrosiveness of phosphate glasses to process equipment and their tendency to devitrify to a chemically less durable product, development efforts shifted to borosilicate glass and related processing equipment.

Early technologies developed to vitrify HLW included (1) a slurry-fed heated canister process (rising level glass process) and (2) calcination in spray, fluid bed, and rotary kiln calciners followed by melting in a metallic melter. The rising level glass process was limited by throughput and exhibited some instabilities; it has been pursued only in India [RAJ-1986]. The French developed the rotary calciner metallic melter process and have constructed the vitrification plants at Marcoule (AVM) and La Hague (AVH). Pilot-plant demonstrations of HLW vitrification were conducted in England [GROVER-1960] in the 1960s and in France [BONNIAUD-1966] and the U.S. [McELROY-1972a] in the early 1970s. Both phosphate and borosilicate glasses were made in demonstration programs in the U.S. [McELROY-1972b], and testing of metallic melters continued in the U.S. in conjunction with the spray calciner until the early 1980s.

Continuous, direct vitrification in a ceramic melting furnace was investigated for the first time in Denmark, where inactive pilot-plant studies were performed at the Riso research establishment beginning in 1962 [BRODERSEN-1966]. This type of vitrification process was not developed further in Denmark, but other countries, including the U.S. and Germany, have developed it to demonstration-scale production. Evaluation of the joule-heated ceramic-lined glass melter began at Pacific Northwest Laboratory (PNL) in 1972. A joule-heated ceramic melter was developed, constructed, and operated to demonstrate industrial application of this technology [CHAPMAN-1980]. The direct liquid feed design of the melter seemed to have the greatest potential for industrial application to continuously producing borosilicate glass given that a separate calcination of the alkaline wastes was not practical.

The first production facility to vitrify HLW was the AVM in Marcoule, France, in 1978 [HWFA-1990; TWT-1991]. This facility continues to operate today. Currently, the world's most mature vitrification technologies are the French AVH process, which is a rotary calciner and metallic melter, and several adaptations of the liquid- or slurry-fed ceramic-lined melter (LFCM). Three countries have committed to development of the LFCM technology: Germany, the U.S., and Japan. In 1979, the Pamela plant began initial vitrification operation at Mol, Belgium, and went radioactive in 1986. In the U.S., the Savannah River Defense Waste Processing Facility (DWPF) will begin radioactive operation in 1995, the West Valley Demonstration Project (WVDP) in 1996, and the Hanford Waste Vitrification Project (HWVP) after the year 2000. Japan's Tokai Vitrification Facility (TVF) and the Japanese Vitrification Facility (JVF) began operations in 1988.

In 1978, an independent panel organized by the American Physical Society [APS-1978] concluded that emplacement of vitrified waste into a geologic repository was likely to provide an adequate solution to the problem of HLW management. Subsequently, DOE's National High-Level Waste Technology Program conducted a review of all options for immobilization of HLW along with assessments of the technology required at the various waste sites [AWS-1979, -1980, -1981]. Research was conducted on 17 candidate waste forms by national laboratories, universities, industrial laboratories, and DOE facilities. An independent review of this research, conducted by the Alternative Waste Form Peer Review Panel [PRP-1980], reduced the list of waste form candidates from fifteen to eight, which were subsequently evaluated for nine scientific and nine engineering parameters affecting the long-term performance and production of waste forms. Finally, these eight candidate waste forms were ranked [PRP-1981] on the basis of a weighted evaluation using leach resistance, waste loading, mechanical strength, radiation stability, and thermal stability as criteria, with leach resistance from 28-day MCC-1 static leach tests receiving the highest weighting factor. In the final ratings, borosilicate glass was rated first and Synroc second [PRP-1981]. Although Synroc appeared to be more durable than borosilicate glass, the ability to process borosilicate glass remotely and the lower processing cost caused it to be favored. Hench et al. [HENCH-1984] summarized the findings of the Peer Review Panel, noting that borosilicate glass rated 2 to 4 times better than Synroc-D (D for defense waste) because of the greater ease of processing. The evaluation method and results, the types and sources of data, and future requirements for waste form evaluation are discussed by Bernadzikowski et al. [BERNADZIKOWSKI-1983]. Although borosilicate glass was rated first, the need for additional work on alternatives such as Synroc was recommended by the Peer Review Panel [LUTZE-1988a].

The potential environmental consequences of selecting borosilicate glass as the waste form for the DWPF were summarized in the Environmental Assessment in 1982 [EA-1982]. It was selected as the reference waste matrix for the Environmental Impact Statements for the DWPF in 1982, the WVDP in 1982, and the HWVP in 1987 [SREIS-1982; WVEIS-1982; HWEIS-1987]. In 1983, a performance assessment study of geologic waste disposal conducted by the National Research Council of the National Academy of Sciences [NAS-1983] concluded among other things that "uncertainties about the physical integrity of borosilicate glass exposed to leaching solutions at high temperatures and uncertainties as to the effect of physical integrity on radionuclide dissolution may require that glass high-level waste be protected from groundwater by a corrosion-resistant overpack when the repository rock is at temperatures greater than 100°C."

In 1990, vitrification of HLW was designated by the U.S. Environmental Protection Agency (EPA) as the Best Demonstrated Available Technology (BDAT) for high-level waste [FR-1990].

1.4 International Experience Overview

A summary of international experience with waste glass is provided in Volume II, Appendix B. A short overview of this experience follows.

Technology for vitrification of HLW has been pursued internationally for more than 40 years. The principal reasons for the international focus on the production of waste glass, particularly on borosilicate waste glasses, are the ease of processing and the relative insensitivity of glass properties to fluctuations in waste composition. The chemical durability of borosilicate glass has also been an important consideration in its choice as a HLW form.

Between 1986 and 1992, various foreign vitrification facilities, in addition to the French AVM facility, began to operate with radioactive waste. Some of these were the Pamela facility in Belgium in 1986, the former Soviet Union EP-500 facility in 1988, the French AVH facility in 1990, Chinese and Indian facilities in 1991, and the British Windscale facility in early 1992. A total of 14 plants (11 in foreign countries), ranging in size from research to pilot plants and full-scale production facilities, are in production or under construction for the conversion of liquid HLW to borosilicate glass [E&S-1982]. Five countries have major industrial-scale reprocessing facilities: France, Japan, United Kingdom, United States, and the former Soviet Union. Also, North Korea has been reported to have completed a reprocessing plant. Other countries purchase reprocessing services from one of these countries, with plans to return the resultant solidified HLW for management in the country of origin. In countries with reprocessing plants, the liquid HLW is stored for a period ranging from one to several tens of years in underground storage tanks. After this storage, the wastes will be (or are being) transferred to a vitrification facility for processing into a canistered, monolithic solid for transport and ultimate disposal.

The current national strategies for managing HLW are summarized in Table 1-2. Included are the location and anticipated quantities of borosilicate glass to be produced by those countries that reprocess spent reactor fuel. In approximately half of the countries listed, borosilicate glass has been selected as the waste form for geologic disposal. France is expected to produce the most waste glass by the year 2030, followed by Japan and the U.S. In the U.S., defense production wastes will account for almost all of the glass to be produced. In other countries, reprocessing of spent fuel from commercial power plants will account for most of the waste glass.

In countries that reprocess spent fuel, special nuclear materials such as uranium and plutonium are either recycled for power reactor fuels or are used in national defense programs. The fission products and processing chemicals that remain after recovery of special nuclear materials are usually liquid slurries defined as liquid HLW. Reprocessing activities have been in progress since the late 1940s and have led to the accumulation of more than 358,000 m³ of liquid HLW in the U.S. alone. Management of such large volumes of waste has been an international concern since the late 1950s. Currently, nearly all liquid HLW is stored in large underground tanks as an interim waste management practice.

Extensive laboratory testing, field testing, glass dissolution modeling, and examination of natural glasses have been conducted as part of many waste management programs worldwide. The scope of the worldwide contributions to our current understanding of borosilicate waste glass corrosion is illustrated by the following:

- Extensive laboratory testing of reference borosilicate glass compositions, (e.g., the Pamela SM58 and SAN60 compositions and the AVM composition designated R7T7 or SON68) (see Appendix A).
- Extensive field testing of reference borosilicate glass compositions under a variety of burial conditions, including field testing programs at Ballidon in the United Kingdom, at Mol in Belgium, at Stripa in Sweden, and at the Waste Isolation Pilot Plant (WIPP) in the U.S. (see Volume II, Section 4.1).

Table 1-2. Worldwide Overview of HLW Management

Country	Waste Form	Vitrification Plant Location (hot startup date)	Glass Production (m ³)	Repository Host Rock	Year to Open Repository
Argentina	Glass	ZAC - Zeiza	1500	Granite	>2010
Belgium	Glass	Pamela - Mol (1986)	850	Clay	2030
Brazil	Spent Fuel	-	-	--	>2020
Canada	Spent Fuel	-	-	Crystalline rock	>2015
China	Glass	Gobi Desert (1991)	160	Granite, tuff, basalt, salt	2030
Finland	Spent Fuel	-	-	Granite	2020
France	Glass	AVM - Marcoule (1978) AVHR7 - La Hague (1990) AVHT7 - La Hague (1993)	5400	Granite, salt, clay, or schist	
Germany	Glass and Spent Fuel	UK and France	2500	Salt	2008
India	Glass	WIP - Tarapur WIP - Trombay WIP - Kalpakkam	1600	Granite or gneiss	>2010
Italy	Glass	IVET - Tricsaia IVEX - Saluggia	600	Clay	2040
Japan	Glass	TVF - Tokai (1993) JVF - Shimokita (1997)	4400	Granite, tuff, mudstone	2030
Netherlands	Glass	UK and France	45	Salt, clay	>2020
South Korea	Glass or Spent Fuel	-	-	Granite	>2010
Spain	Spent Fuel	-	-	Granite, salt	2020
Sweden	Spent Fuel	-	-	Crystalline rock	2020

Country	Waste Form	Vitrification Plant Location (hot startup date)	Glass Production (m ³)	Repository Host Rock	Year to Open Repository
Switzerland	Glass	UK and France	1200	Granite or sediment. rock	2025
Taiwan	Spent Fuel	-		Granite, shale, or mudstone	--
United Kingdom	Glass	WVP (1992) Sellafield	1600	Crystalline rock	>2040
United States	Glass and Spent Fuel	DWPF - So. Carolina (1995) WVDP - New York (1996) HWVP - Wash. CWPF - Idaho	3300 210	Tuff	2010
Soviet Union (Former)	Glass	Kyshtym Krosnyarsk (shutdown)	1200	Salt, granite, clay, gneiss	--

- Modeling of waste glass corrosion at the Hahn-Meitner Institute in Berlin. Grambow [GRAMBOW-1985] proposed a geochemical model based on transition-state theory that explained the observed behavior of several different waste glasses in laboratory tests. The Grambow model has been applied to the study of natural basalt glasses from the deep ocean [GRAMBOW-1986c], alteration of basalt glass in seawater [CROVISIER-1986], and HLW glass in contact with bentonite clay [JSS-1988]. A similar approach is being used to study the dissolution behavior of French and U.S. HLW glass [ADVOCAT-1990; BOURCIER-1990b] and has been integrated in a performance assessment model for a repository in Japan [McGRIL-1990]. The modeling of HLW glass dissolution is discussed in detail in Section 3.3.

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2.0 DESCRIPTION OF BOROSILICATE WASTE GLASS AND ENVIRONMENTAL CONDITIONS OF INTEREST

The corrosion rate of HLW borosilicate glass depends on both the characteristics of the glass and the environmental conditions to which it is exposed. For the U.S. HLW, neither the waste form products nor the environmental conditions to which these products will be exposed can yet be precisely defined. The vitrification facilities have not started production, and the location of the geological repository has not been finalized. The intent of this section, therefore, is to orient the reader concerning the range of waste glass products and potential environmental conditions that are of interest for testing and modeling. Section 2.1 describes the target composition ranges, the reference waste glass compositions that have been established for testing, and other characteristics to be controlled during production. The plausible environmental conditions to which the waste glass may be exposed during storage, transportation, and eventual disposal in a geologic repository are discussed in Section 2.2.

2.1 Description of Waste Glass Products

The important characteristics of the waste glass products to be produced by the DWPF, WVDP, and HWVP include the composition, radioactivity, dose rate, and heat generation rate for each canistered waste form. Other important characteristics include redox state, level of crystallinity, surface area, and homogeneity. Section 2.1.1 describes the target glass compositional regimes and the nominal or reference waste glass compositions that are expected to be produced; other reference borosilicate glass waste form compositions that have been used for testing are summarized in Appendix A. Section 2.1.2 describes other waste glass characteristics, including redox state (2.1.2.1), changes that occur during cooldown of the melt (2.1.2.2), and the heat generation and radioactivity associated with the canistered waste (2.1.2.3).

2.1.1 Waste Glass Compositions

The target composition range for DWPF glass is shown, in Table 2-1. Reference chemical compositions of four waste glasses to be produced at the Savannah River Site and the design basis composition are shown in Table 2-2 [SRWCP-1992]. The target composition range for the WVDP glass is shown in Table 2-3 [WVWCP-1991]; within this range, the nominal final waste form composition for West Valley glass and the nominal blending of components to achieve this composition are as shown in Table 2-4. The target compositional range for the HWVP glass remains to be established. Other reference waste glass compositions that have been used for testing purposes worldwide are shown in Appendix A. The composition similarities between reference borosilicate glass compositions can be illustrated by plotting the amount of network formers, modifiers, and intermediates (all as oxides) in each glass on a ternary diagram as shown in Fig. 2-1 [RAMSEY-1989].

2.1.2 Other Waste Glass Characteristics

2.1.2.1 Redox State

Most U.S. HLW glasses contain a significant amount of iron oxide; the valence state of the iron is indicative of the oxidation/reduction conditions which existed during melting. The redox state of a glass can be indicated by the $(\text{Fe}^{2+}/\text{total Fe})$ ratio or by the $(\text{Fe}^{2+}/\text{Fe}^{3+})$ ratio [ASTM-1992]. A redox ratio of zero indicates a totally oxidized glass, and a very high ratio indicates a very reduced

Table 2-1. Target Composition Range for DWPF Waste Glass

Component	Range (wt. %)	
	Minimum	Maximum
SiO ₂	44.6	54.4
Al ₂ O ₃	2.9	7.1
B ₂ O ₃	6.9	10.2
CaO	0.8	1.2
MgO	1.3	1.5
Na ₂ O	8.2	12.1
K ₂ O	2.1	4.6
Li ₂ O	3.1	4.6
Fe ₂ O ₃	7.4	12.7
MnO	1.6	3.1
TiO ₂	0.6	1.0
U ₃ O ₈	0.5	3.2
ThO ₂	0.01	0.8
Group A ^a	0.08	0.2
Group B ^b	0.08	0.9

^aIsotopes of Tc, Se, Te, Rb, and Mo.

^bIsotopes of Ag, Cd, Cr, Pd, Ti, La, Ce, Pr, Pm,
Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, and Cm.

Table 2-2. Reference DWPF Waste Glass Compositions

Component	Composition (wt.%)				
	Batch 1	Batch 2	Batch 3	Batch 4	Blend ^a
SiO ₂	49.8	50.2	50.0	49.3	50.2
B ₂ O ₃	7.7	7.7	7.7	8.1	8.0
Al ₂ O ₃	4.9	4.5	3.2	3.3	4.0
Fe ₂ O ₃	12.5	10.6	11.2	11.3	10.4
Na ₂ O	8.6	8.6	8.5	8.9	8.7
K ₂ O	3.5	3.5	3.5	4.0	3.9
Li ₂ O	4.4	4.4	4.4	4.3	4.4
U ₃ O ₈	0.5	2.3	3.2	0.8	2.1
CaO	1.2	1.0	0.9	0.8	1.0
MgO	1.4	1.4	1.4	1.4	1.4
ThO ₂	0.4	0.6	0.8	0.2	0.2
Group A ^b	0.1	0.1	0.1	0.2	0.1
Group B ^c	0.2	0.4	0.2	0.6	0.4
MnO	2.1	1.6	1.8	3.1	2.0
CuO	0.4	0.4	0.4	0.5	0.4
TiO ₂	0.7	0.7	0.7	1.0	0.9
NiO	0.8	0.9	1.1	1.1	0.9
Cr ₂ O ₃	0.1	0.1	0.1	0.1	0.1
Other	0.7	1.0	0.8	1.0	0.9

^aThe "blend" is the current DWPF design-basis glass.

^bIsotopes of Tc, Se, Te, Rb, and Mo.

^cIsotopes of Ag, Cd, Cr, Pd, Ti, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, and Cm.

Table 2-3. Target Composition Range for WVDP Glass

Component	Range (wt. %)	
	Minimum	Maximum
SiO ₂	38.8	43.2
B ₂ O ₃	11.0	14.8
K ₂ O + Li ₂ O + Na ₂ O	14.7	18.8
Fe ₂ O ₃	10.2	13.8
Al ₂ O ₃	5.4	6.6
BaO + CaO + MgO	1.2	1.6
MnO	0.7	0.9
P ₂ O ₅	0.0	4.0
ThO ₂	3.0	4.1
UO ₃	0.5	0.7
ZrO ₂	1.1	1.5
Other ^a	1.0	8.0

^aIncludes CeO₂, Cr₂O₃, Cs₂O, CuO, La₂O₃, MoO₃, Nd₂O₃, NiO, PdO, Pr₆O₁₁, Rh₂O₃, RuO₂, SnO₂, TeO₂, Y₂O₃, and ZnO.

Table 2-4. Nominal Oxide Content of WVDP Glass

Oxide	Purex (19.2%)	+ Thorex (4.6%)	+ Zeolite ^a (17.4%)	+ Cold Chemical Oxides (58.8%)	= Final Comp. (%)
SiO ₂	7.8	0.3	46.0	53.5	41.0
B ₂ O ₃	0	1.2	0	21.8	12.9
Fe ₂ O ₃	57.6	12.9	2.4	0	12.1
Na ₂ O	7.6	1.1	13.9	6.9	8.0
K ₂ O	0	0.6	23.5	1.5	5.0
Li ₂ O	0	0	0	6.3	3.7
Al ₂ O ₃	4.5	4.6	11.9	4.9	6.0
CaO	1.9	0.0	0.6	0	0.5
MgO	0.4	0.0	0.5	1.2	0.9
MnO	3.0	0.2	0	0.4	0.8
P ₂ O ₅	6.2	0.0	0	0	1.2
ThO ₂	0	78.9	0	0	3.6
TiO ₂	0	0	0.4	1.2	0.8
UO ₂	3.0	0.0	0	0	0.6
ZrO ₂	0	0	0	2.2	1.3
Other ^b	8.1	0	0.8	0	1.7

^aIncludes radioactive Cs.^bConstitutes other components each present at less than 0.5 wt.%.

Fig. 2-1. Ternary Diagram Depicting Compositional Similarities for a Variety of Glasses that were Tested in the Waste Isolation Pilot Plant (WIPP) (adapted from [RAMSEY-1989]).

glass. From a processing standpoint, the redox state in the DWPF melter must be slightly reducing to minimize foaming [PLODINEC-1982, -1986]. Originally Jantzen et al. recommended an ($\text{Fe}^{2+}/\text{Fe}^{3+}$) target ratio of 0.1 to 0.5 as being optimal for DWPF [JANTZEN-1986a]; however, a narrower, only slightly reducing range of 0.1 to 0.2 is now preferred. The redox state in the DWPF melter will be controlled through the redox state of the melter feed. The feed will be made more reducing by adding formic acid or more oxidizing by adding nitric acid.

Redox conditions in the melter can affect the precipitation of crystalline phases in the molten glass. Spinels, e.g., NiFe_2O_4 , are crystalline phases that form only if the glass is held below its liquidus temperature. Some waste components (noble metals Ru, Rh, and Pd) do not dissolve in glass but are encapsulated in the glass matrix. Alkali, alkaline earths, copper, sulfates, selenates, tellurates, and phosphates can react to form conductive phases that can accumulate in the molten glass. The accumulation of conductive noble metal and crystalline phases in the melter could cause an electrical short and limit the melter lifetime.

The tendency of borosilicate waste glasses to crystallize after pouring varies with redox state of the glass. Bickford et al. [BICKFORD-1984] and Jantzen [JANTZEN-1984a] found that at reduced oxygen fugacity, SRL TDS 165 waste glasses containing 5 to 9 wt.% Fe_2O_3 and 0.09 wt.% RuO_2 had less tendency to crystallize than at higher oxygen fugacity. Crystallization was detected by X-ray diffraction, scanning electron microscopy, and nuclear magnetic resonance. In contrast, Buechele et al. [BUECHELE-1990] reported that for WVDP simulated waste glass SF-12 containing 11.3 wt.% Fe_2O_3 but no noble metals, both very reduced ($\text{Fe}^{2+}/\text{Fe}^{3+} > 1.8$) and very oxidized (< 0.01) glasses crystallized less than glasses with an intermediate redox state (0.45). The laboratory samples tested were heat treated for as long as 100 hours at 700°C , which is much longer than would be expected for a production-sized canister of glass. Jain et al. [JAIN-1991] reported that more reduced glasses tended to be more crystalline than more oxidized ones, although the maximum crystallinity was only 1.4 vol.%. Overall, it appears that glass crystallization is affected somewhat by redox conditions, but the magnitude of the effect depends on the waste glass composition. In addition to foaming and devitrification, glass properties such as chemical durability [FENG-1989a, MANARA-1985] and viscosity [FENG-1989a] of high-iron glasses depend on redox. The effects of crystallization on the durability of waste glass are discussed in Volume II, Section 2.2.2.

2.1.2.2 Characteristics Produced during Cooldown

Figure 2-2 shows a typical DWPF canister which nominally contains about 1700 kg of waste glass. At the nominal fill rate of ~ 100 kg/hr, about 17 hours are required to fill each canister. Edwards [EDWARDS-1987] and Marra et al. [MARRA-1992b] studied the rate of cooling of DWPF canisters after filling with molten glass and found that a period of 16 to 17 hours was required for the centerline temperature to decrease to less than 500°C . After pouring the vitrified waste, about 36 hours are required for the filled canisters to cool to below 100°C [EDWARDS-1987; MARRA-1992a]. Cooling of the molten waste glass in a canister can result in several changes, including (1) crystallization, (2) glassy phase separation, and (3) cracking. Figure 2-3 is a schematic showing the general temperature regime for each of these phenomena.

Fig. 2-2
Schematic of the DWPF Canistered Waste
Showing Nominal Physical Characteristics

Fig. 2-3. Temperature Ranges that Correspond to Potential Changes in Waste Glass Physical Properties

2.1.2.2.1 Crystallization

Jantzen et al. [JANTZEN-1985] showed that slow cooling (25°C/h) of a canister filled with waste glass through the temperature range of 950 to 550°C caused crystallization of the glass. Robnett et al. [ROBNETT-1981] found that crystallization occurred from 900 to 500°C. Marra et al. [MARRA-1992b] measured a maximum of 3.6 vol.% crystallinity in canisters containing simulated DWPF waste glass. In a study of the devitrification of laboratory samples of waste glasses resulting from heat treatments simulating the expected cooling of filled canisters, Buechele et al. [BUECHELE-1991b] found a maximum of less than 2 vol.% crystals in WVDP glasses. Jain et al. [JAIN-1991b] studied the degree of crystallization of production-sized canistered waste forms of three WVDP glasses filled under four pouring rates followed by normal convective cooling. The largest amount of crystals observed was 2.3 vol.%, with no significant difference attributed to pouring rate. Thus, natural convective cooling after filling appears to result in sufficiently rapid cooling of the waste form to prevent the formation of appreciable amounts of crystalline material. The effects of crystallization on the durability of waste glass are discussed in Volume II, Section 2.2.2.

2.1.2.2.2 Cracking/Surface Area

After filling, the canistered waste glass will cool in air via radiative and convective cooling. Edwards [EDWARDS-1987] found that 33 to 36 hours are required for the surface temperature of filled canisters to decrease to less than 100°C. As the waste form cools, it can crack, resulting in a greater surface area compared with that of the unfractured monolith. The greatest stress on the borosilicate glass during normal production operations will result from temperature changes during cooling [KIENZLER-1989]. The surface area of the waste form will be primarily a function of the cooling rate of the glass after pouring. Stresses in glass can be relieved by viscous flow above the glass transition temperature, so that cracking can occur only below the glass transition temperature. The glass transition temperature of U.S. borosilicate waste glasses is 430 to 450°C [MARRA-1992a], so cracking can occur only below about 450°C. In addition to axial and radial cooling stresses within the waste form, hoop stresses will also develop in the canister and, in turn, in the waste form because of the differential thermal expansion (contraction) between these materials.

Slate et al. [SLATE-1978] calculated that the maximum increase in surface area of the glass during cooling was a factor of 34 over that of the initial monolith. Ross et al. [ROSS-1979] studied the increase in surface area as a function of cooling rate and found that with air cooling of intermediate-scale canisters (5-ft high by 0.5-ft diameter) the surface area increased by about a factor of ten. Martin [MARTIN-1985] also studied the fracturing of half-scale canistered waste forms under three cooling conditions--air cooling, insulated cooling, and water quenching. The surface area increases were a factor of 46, 21, and 24, respectively, with the largest increase corresponding to the conditions expected in practice. Peters et al. measured the surface area of full-scale DWPF canistered waste forms (10-ft high by 2-ft diameter) that were cooled over a period of 50 hours and found that the surface area increased by a factor of 18 [PETERS-1981].

2.1.2.2.3 Glassy Phase Separation

Separation into two separate glassy phases has been found to occur in borosilicate glasses. Such separation is the basis for the useful characteristics of commercial glasses such as PyrexTM and VycorTM which were developed by Corning, Inc. There are two basic types of glass-in-glass phase separation. In one type, the microstructure of the separated glass consists of droplets of one phase in a matrix of the other phase. If the matrix is more durable than the original (nonphase-separated glass),

the phase-separated glass will be more durable than the original. If the matrix glass is less durable than the original, then the phase-separated glass will be less durable than the original. The second type of phase separation consists of two separate, continuously interconnected phases. Such a structure will always result in a less durable glass after phase separation. Since in an industrial scale operation it is difficult to control which type of phase separation occurs, it is best to formulate the glass composition to try to avoid phase separation.

Many investigators have looked unsuccessfully for glassy phase separation (separation into two distinct glassy phases) in borosilicate waste glass. Engell et al. [ENGELL-1982] investigated the tendency of two Swedish HLW glasses to phase separate. Phase separation occurred only if the waste compositions were modified to contain much higher levels of B_2O_3 . Palmiter et al. [PALMITER-1991] studied three WVDP simulated waste glasses and found no evidence of phase separation. Others [JANTZEN-1984a; BUECHELE-1990, -1991a, -1991b] have studied the microstructure of heat-treated, simulated waste glasses and observed no evidence of phase separation. These studies indicate that glassy phase separation is not expected to occur in properly formulated borosilicate waste glasses.

2.1.2.3 Canistered Waste Heat Output and Radioactivity

Table 2-5 shows heat generation, radioactivity, and gamma dose rates for a DWPF reference glass [SREIS-1982; PLODINEC-1982], the WVDP glass [WVWCP-1991], and four HWVP glasses [HWPWF-1991]. The composition and age of the waste and the waste loading determine these parameters. The radioactivity of individual radionuclides in the canistered DWPF waste at selected times is shown in Volume I, Appendix B. Because one of the stated objectives of this document (see Section 1.1.1) is to "address the rates and forms (solutes and colloids) in which radionuclides are released from corroding waste glass into contacting water," it is necessary to identify the "important" radionuclides in the list presented in Volume I, Appendix B.

Several approaches have been used to identify the "important" or "key" radionuclides in borosilicate glass waste [KERRISK-1985a; SCP-1988]. Unfortunately, somewhat different lists are obtained depending on how "importance" is established. The following is intended to provide some perspective on potentially important radionuclides while avoiding too much digression to discuss the relative merits of the various measures of "importance".

Kerrisk [KERRISK-1985a] has identified lists of important radionuclides based on utilizing (1) the fractional contribution to the total radioactivity inventory over time, (2) the ratio of the inventory to the EPA 40 CFR 191 limit for release to the accessible environment (referred to as the EPA release limit) [EPA-1985], (3) the ratio of a model-calculated dissolution rate to the EPA limit, and (4) a comparison of a model-calculated dissolution rate to the NRC controlled release rate performance objective for the engineered barrier system (referred to hereafter as the NRC release rate limit) [NRC-1986]. The Yucca Mountain site characterization plan [SCP-1988, pp. 151-161] includes an identification of the important radionuclides in WVDP and DWPF waste based on the ratio of NRC release rate limit to one part in 100,000 of the 1000-year inventory. In addition, important radionuclides have been identified based on their contribution to calculated doses in performance assessment studies [NAS-1983, pp. 248-296]. Because the model dependent approaches give results that are dependent on the models and assumptions used, the focus here is on the model-independent approaches (i.e., approaches 1 and 2 utilized by Kerrisk and the SCP approach).

Table 2-5. Heat Generation, Radioactivity, and Gamma Dose Rates for DWPF, WVDP, and HWVP Reference Waste Glasses^a

Waste Glass Type	Heat Generation (W/canister)	Radioactivity (kCi/canister)	Gamma Dose Rate ^c (R/h)
DWPF	<752	<235	5,570
WVDP	326	110	7,500
HWVP ^b			
NCAW	614	271	13,400
CC	125	42	1,900
PFP	5.8	0.5	700
NCRW	1.3	0.1	4,600

^aAll values are indexed to the year 2000, except for the DWPF values which are calculated at the time of production beginning in 1994.

^bNote: because processing options for the Hanford wastes have not been finalized these data should be considered preliminary.

^cThese are the dose rates at the canister surface.

The radioactivity (expressed in curies) as a function of time after disposal of various radionuclides is one measure of the importance of each radionuclide. The percentages of total radioactivity contributed by each radionuclide at 10^2 to 10^5 years [KERRISK-1985a], which are shown in Table 2-6, are useful for identifying radionuclides that are potentially important at various times after disposal.

Another approach to identifying important radionuclides is to compare the inventories at various times with the EPA 40 CFR 191 cumulative release limits at the boundary of the accessible environments. In Table 2-7, the radionuclides are ordered by the ratio of the inventory to the EPA release limits [KERRISK-1985a]. In general, this approach accentuates the importance of the actinides because of the lower EPA release limits for alpha-emitting radionuclides. It is instructive to note, however, that while ^{237}Np can be considered to be the most important isotope for compliance with the 10 CFR 60 controlled release rate requirements at 10,000 years (see discussion below), it is comparatively less important for compliance with the EPA standard for the cumulative release at the boundary of the accessible environment.

The fraction of the postclosure inventory of individual radionuclides that can be released per year from the engineered barrier system in a repository is the most directly relevant approach since the regulatory performance objective involved applies to the EBS subsystem. For the WVDP waste, Table 2-8 shows the fractions of the individual radionuclide inventory that could be released per year from the engineered barrier system at 1000 years and at 10,000 years after repository closure [SCP-1988, pp. 7-155]. In this table, the release rate limit is calculated separately for the West Valley waste. All radionuclides whose inventories are great enough that they could not be released in a single year at 1000 years after closure are included, and those for which the release rate must be

Table 2-6. Radionuclide and Percent of Total Radioactivity for Various Decay Times

	10 ² Years (%)	10 ³ Years (%)	10 ⁴ Years (%)	10 ⁵ Years (%)
⁹⁰ Sr/ ⁹⁰ Y	50	--	--	--
¹³⁷ Cs/ ^{137m} Ba	46	--	--	--
²³⁸ Pu	3	1	--	--
⁶³ Ni	0.7	0.6	--	--
¹⁵¹ Sm	0.7	--	--	--
²⁴¹ Am	0.2	31	--	--
²⁴¹ Pu	0.07	--	--	--
²³⁹ Pu	0.05	28	43	6
²⁴⁰ Pu	0.03	16	13	--
⁵⁹ Ni	--	6	11	8
⁹⁹ Tc	--	6	11	24
⁹³ Zr/ ^{93m} Nb	--	6	14	22
²³⁴ U	--	2	5	6
¹²⁶ Sn	--	0.4	0.8	1
⁷⁹ Se	--	--	0.5	0.4
¹³⁵ Cs	--	--	0.5	1
²³⁰ Th	--	--	0.4	4
²²⁶ Ra	--	--	--	4 ^a

^aDecay products of ²²⁶Ra are in secular equilibrium; each decay product also represents 4% of the inventory.

Source: Adapted from [KERRISK-1985a].

Table 2-7. Defense High-Level Waste Radionuclides Ordered by Ratio of Inventory to EPA Limit

	Radionuclide and (Inventory/EPA Limit) for Various Decay Times						
	10 ² Year		10 ³ Year		10 ⁴ Year		10 ⁵ Year
²³⁸ Pu	8.7 x 10 ³	²⁴¹ Am	1.9 x 10 ²	²³⁹ Pu	1.3 x 10 ²	²³⁰ Th	7.5 x 10 ¹
⁹⁰ Sr/ ⁹⁰ Y	7.8 x 10 ³	²³⁹ Pu	1.7 x 10 ²	²⁴⁰ Pu	3.8 x 10 ¹	²³⁴ U	1.1 x 10 ¹
¹³⁷ Cs/ ^{137m} Ba	7.4 x 10 ³	²⁴⁰ Pu	9.9 x 10 ¹	²³⁴ U	1.4 x 10 ¹	²³⁹ Pu	9.7
²⁴¹ Am	7.8 x 10 ²	²³⁴ U	1.5 x 10 ¹	²³⁰ Th	1.3 x 10 ¹	²²⁶ Ra ^a	7.4
⁶³ Ni	4.3 x 10 ²	²³⁸ Pu	7.1	⁵⁹ Ni	3.3	⁹³ Zr/ ^{93m} Nb	1.9
¹⁵¹ Sm	2.1 x 10 ²	⁵⁹ Ni	3.5	⁹³ Zr/ ^{93m} Nb	2.0	⁵⁹ Ni	1.4
²³⁹ Pu	1.7 x 10 ²	⁹³ Zr/ ^{93m} Nb	2.0	²²⁶ Ra ^a	9.7 x 10 ⁻¹	²³⁶ U	6.3 x 10 ⁻¹
²⁴⁰ Pu	1.1 x 10 ²	²³⁰ Th	1.2	²³⁶ U	6.2 x 10 ⁻¹	²³⁷ Np	2.6 x 10 ⁻¹
²⁴¹ Pu	2.4 x 10 ¹	²³⁶ U	6.0 x 10 ⁻¹	⁹⁹ Tc	3.3 x 10 ⁻¹	⁹⁹ Tc	2.4 x 10 ⁻¹
		⁹⁹ Tc	3.4 x 10 ⁻¹	²³⁷ Np	2.7 x 10 ⁻¹	²³⁸ U	1.5 x 10 ⁻¹

^aDecay products of ²²⁶Ra are in secular equilibrium.

Source: [KERRISK-1985a]

Table 2-8. Important Radionuclides in West Valley Waste^a

Isotope	Half Life (y)	1000-Yr Postclosure Inventory ^c (Ci)	10,000-Yr Inventory (Ci)	NRC Release Rate Limit per Year (Ci)	Allowed Fractional Release Rate Per Year at 1000 y	Allowed Fractional Release Rate Per Year at 10,000 y
<u>C-14^b</u>	5,730	1.22E+02	4.1E+01	1.22E-03	1.0E-05	3.0E-05
<u>Ni-59</u>	76,000	8.12E+01	7.5E+01	8.12E-04	1.0E-05	1.1E-05
Ni-63	100	4.04E+00	--	2.13E-04	5.4E-05	1.0
<u>Se-79</u>	65,000	3.66E+01	3.3E+01	3.66E-04	1.0E-05	1.1E-05
<u>Zr-93/ Nb-93m</u>	1.5E+06/ 13.6	2.30E+02	2.3E+02	2.30E-03	1.0E-05	1.0E-05
<u>Tc-99</u>	2.13E+05	1.59E+03	1.5E+03	1.59E-02	1.0E-05	1.1E-05
Pd-107	6.5E+06	1.20E+00	1.2E+00	2.13E-04	1.8E-04	1.8E-04
<u>Sn-126/ Sb-126m/ Sb-126</u>	1.0E+05/ 0.001/ 0.034	3.97E+01	3.7E-01	3.97E-04	1.0E-05	1.1E-05
I-129	1.6E+07	3.60E-01	3.6E-01	2.13E-04	5.9E-04	5.9E-04
<u>Cs-135</u>	3.0E+06	1.60E+02	1.6E+02	1.60E-03	1.0E-05	1.0E-05
<u>Sm-151</u>	90	5.85E+01	--	5.85E-04	1.0E-05	1.0
Pb-210	22.3	1.10E-02	5.2E-01	2.13E-04	2.1E-02	4.1E-04
Ra-226	1,600	1.27E-02	4.9E-01	2.13E-04	1.7E-02	4.3E-04
Ra-228	5.76	1.17E+00	2.1E+00	2.13E-04	1.8E-04	1.0E-04
Ac-227	21.773	2.00E-03	2.2E-02	2.13E-04	1.1E-01	9.7E-03
Th-229	7,300	9.55E-01	6.00E+00	2.13E-04	2.2E-04	3.5E-05
Th-230	75,400	6.65E-02	6.2E-01	2.13E-04	3.2E-03	3.4E-04
Th-232	1.4E+10	1.60E+00	1.6E+00	2.13E-04	1.3E-04	1.3E-04
Pa-231	32,800	2.23E-03	2.1E-02	2.13E-04	9.5E-02	1.0E-02

Table 2-8 (Contd.)

Isotope	Half Life (y)	1000-Yr Postclosure Inventory ^c (Ci)	10,000-Yr Inventory (Ci)	NRC Release Rate Limit per Year (Ci)	Allowed Fractional Release Rate Per Year at 1000 y	Allowed Fractional Release Rate Per Year at 10,000 y
U-233	1.59E+05	9.95E+00	9.6E+00	2.13E-04	2.1E-05	2.2E-05
U-234	2.45E+05	7.16E+00	7.0E+00	2.13E-04	3.0E-05	3.0E-05
U-235	7.04E+08	1.02E-01	1.0E-01	2.13E-04	2.0E-03	2.1E-03
U-236	2.34E+07	3.40E-01	3.4E-01	2.13E-04	6.3E-04	6.3E-04
U-238	4.47E+09	8.50E-01	8.5E-01	2.13E-04	2.5E-04	2.5E-04
<u>Np-237^d</u>	2.14E+06	2.33E+01	2.61E+01	2.13E-04	1.0E-05	8.9E-06
Pu-238	87.74	1.60E+00	--	2.13E-04	1.3E-04	1.0
<u>Pu-239</u>	24,110	1.65E+03	1.3E+03	1.65E-02	1.0E-05	1.3E-05
<u>Pu-240</u>	6,560	1.22E+03	4.7E+02	1.22E-02	1.0E-05	2.6E-05
Pu-241	14.35	8.12E+00	--	2.13E-04	2.6E-05	1.0
Pu-242	3.76E+05	1.70E+00	1.7E+00	2.13E-04	1.2E-04	1.3E-04
<u>Am-241</u>	432	1.36E+04	7.3E-03	1.36E-01	1.0E-05	1.0
Am-242m	141	1.12E-01	--	2.13E-04	1.9E-03	1.0
<u>Am-243</u>	7,370	2.17E+03	9.3E+02	2.17E-02	1.0E-05	2.3E-05
Cm-245	8,500	9.17E+00	4.4E+00	2.13E-04	2.3E-05	4.8E-05
Cm-246	4,780	3.68E+00	1.0E+00	2.13E-04	5.8E-05	2.1E-04

^aSource: adapted from [SCP-1988].

^bRadionuclides with a release that must be controlled at 1 part in 100,000 of their own 1,000 year postclosure inventory are underlined.

^cE indicates exponential notation.

^dGrow-in from decay of ²⁴¹Am increases the inventory of this isotope between 1000 and 10,000 years.

controlled at 1 part in 100,000 of their own 1000-year postclosure inventory [NRC-1986] are underlined. If the fraction of the inventory that can be released from the engineered barrier system is viewed as a measure of importance then a comparison of the allowable release rate fractions at 1000 years and at 10,000 years after closure of the repository shows that the relative importance of radionuclides changes with time. For example, it is instructive to note that while it is important to control the release rate of ^{241}Am at 1000 years after closure, control of its release rate at 10,000 years after closure is unimportant (at this point in time, all of the remaining inventory can be released in one year). On the other hand, while ^{237}Np may appear to be unimportant because it makes a negligible contribution to the total inventory at 10,000 years (see Table 1-1), it can be viewed as the most important isotope for compliance with the NRC controlled release rate performance objectives at 10,000 years after closure of the repository because the allowed fractional release rate at this point in time is actually lower than $10^{-5}/\text{yr}$ due to grow-in (from radioactive decay of ^{241}Am) between 1000 and 10,000 years.

Based on an assessment of how radionuclides that may reach the environment within 10,000 years after waste disposal contribute to dose to individuals, the principal contributors were C-14, Cs-135, Np-237, Pb-210, and Se-79 [NAS-1983, pg. 11]. This is a subset of the important radionuclides in Table 2-8. Likewise, with a few exceptions, the lists in Tables 2-6 and 2-7 are also subsets of the list in Table 2-8. Table 2-8 will therefore be used as the primary basis for identifying important radionuclides in this document. It shows that the important radioelements are the actinides (principally Am, Pu, Np, and U) as well as some of the fission and activation product radioelements (principally, Sr, Cs, C, Ni, Zr, Tc, Th, Ra, and Sn) [KERRISK-1985a]. The fractions of the radioisotopes of these elements that can be released annually (see Table 2-8) can be used as an indicator of their relative importance.

2.2 Environmental Conditions of Interest

The environmental conditions to which the U.S. waste glass may be exposed cannot yet be precisely defined because neither the geologic repository setting nor the designs of the engineered systems for handling, storage, transportation, and disposal have been finalized. However, the conditions that have been identified as a result of analysis of candidate repository concepts provide an indication of the types of conditions that are "plausible." Although the term plausible is imprecise, its usage here is consistent with earlier efforts [CLAIBORNE-1987] to communicate, in an approximate way, the types of conditions that are of interest in considering waste glass corrosion processes. In this document, plausible conditions during handling, storage, and transport are discussed in Section 2.2.1. Disposal conditions for saturated and unsaturated geologic settings are summarized in Sections 2.2.2 and 2.2.3, respectively.

2.2.1 Conditions during Storage and Transportation

Sealed, decontaminated canisters will be stored prior to transport to a U.S. geological repository. Because the transport of canistered waste to a repository in the U.S. probably will not begin until at least 2015 [MISSION PLAN-1991], the filled canisters could be stored at the vitrification sites for 15 to 20 years or longer.

During transport within the vitrification facilities and in temporary storage, the canistered waste forms could be affected by increased temperatures resulting from heat generated through radioactive decay, by self-irradiation, and by internal and external stresses. Because the canisters will be welded shut and water must be excluded [WAPS-1993], the waste glass will not be affected by

humidity conditions external to the canister. However, the waste glass will be exposed to the gas that occupies the canister volume above the glass level. The temperature, stresses, and fill gas conditions to which the waste glass may be exposed during storage and transportation are discussed briefly in Sections 2.2.1.1 through 2.2.1.3, together with the effects that are expected as a result of such exposure. The effects of self-irradiation are discussed in Volume II, Section 2.5.

2.2.1.1 Temperature during Storage and Transportation

The "Waste Acceptance Product Specifications" (WAPS) require that after initial cooldown, the temperature of canistered waste form must not exceed 400°C [WAPS-1993]. For U.S. waste glass, the glass transition temperature is about 430 to 450°C [MARRA-1992a]. During storage, the canisters will be kept below the glass transition temperature to prevent changes in phase structure. The glass transition temperature can vary by about 10°C depending on the cooling rate. If the WAPS maximum storage temperature of 400°C is not exceeded, then, regardless of the cooling rate, the waste glass will remain below the glass transition temperature. Following cooldown, the canisters will be kept in freely circulating air. In storage, the canisters will be kept either in freely circulating air or in individual storage cells. Where individual storage cells are used, natural or forced convection may be employed to ensure that temperature limits are not exceeded [WAPS-1993].

Palmiter et al. [PALMITER-1991] and Malow [MALOW-1989] have reported that heat treatment of simulated HLW glasses for up to a hundred hours at temperatures below the glass transition temperature resulted in no changes in phase structure. By maintaining the temperature below 400°C to satisfy the WAPS, the phase structure of the glass should remain unchanged during transport within the vitrification facilities, in temporary storage, and during transport to the repository.

2.2.1.2 Canister Fill Gas

Internal pressure in the canisters must not exceed 21 psia [WAPS-1993]. Harbour [HARBOUR-1990] studied the volatility of glass components in the canistered waste form and concluded that no gases would be released during normal handling or storage. The internal gas pressure measured by Harbour et al. [HARBOUR-1991] in four sealed, glass-filled DWPF canisters was always slightly less than atmospheric, and the relative humidities at ambient temperature were less than 20%. At such low relative humidities, the effects of the fill gas on the waste glass are expected to be minimal (see discussion of the effects of humidity on waste glass weathering in Volume II, Section 3).

2.2.2 Disposal Conditions in Saturated Geologic Environments

Following emplacement in a geologic repository, the canistered waste glass will initially be isolated from the repository host rock and groundwater environment not only by the canister but also by engineered containment barriers. Until these barriers are breached, the waste glass environment inside the canister will be similar to that discussed in Section 2.2.1, although the temperature conditions will now be determined by the heat dissipation rate into the surrounding engineered barriers and host rock. After the containment barriers are eventually breached, the waste glass will interact with any fluid that penetrates the breach openings (groundwater for saturated settings and groundwater or air and water vapor mixtures for unsaturated settings). The corroding glass system is illustrated schematically in Fig. 1-3.

The temperature conditions to which the waste glass may be exposed subsequent to emplacement in a repository are summarized in Section 2.2.2.1; the pressure, hydrological, and geochemical conditions that are plausible for the immediate vicinity of the glass (i.e., for Region 4 in Fig. 1-3) following breaching of the containment barriers are summarized in Sections 2.2.2.2, 2.2.2.3, and 2.2.2.4, respectively. It was assumed that the host rock and repository openings in saturated settings will have returned to hydraulically saturated conditions prior to breaching of the engineered barriers; if breaches were to occur prior to resaturation, the unsaturated conditions to which the waste glass would be exposed would be similar to those discussed in Section 2.2.3.

2.2.2.1 Temperature

The temperature conditions that the waste glass will experience can be calculated fairly accurately once the design parameters are established. Temperature conditions in salt, basalt, and other host rock formations were analyzed for the Salt Repository Program [SRP-1987], the Basalt Waste Isolation Project [BWIP-1987], and the Sedimentary Rock Evaluation Program [CROFF-1986]. These analyses showed that, following emplacement, the waste glass temperature will rise initially, reach a peak temperature after a few decades, and thereafter decrease slowly and monotonically until it approaches the host rock ambient temperature several thousand years after emplacement. The peak temperatures calculated for glass waste packages in salt and basalt were approximately 80°C [SRP-1987; BWIP-1987]. Unfortunately, these results were based on analysis of waste packages with thermal outputs of 470 W and 225 W for salt and basalt, respectively, which are lower than some of the heat generation rates identified in Table 2-5 (Section 2.1.2.3). Peak temperatures approaching 300°C have been calculated for 2210 W waste packages in sandstone, shale, anhydrite, and carbonate host rocks [CROFF-1986]; although this is a much higher thermal output than currently expected (see Table 2-5), the glass temperatures were estimated to drop below 150°C before the end of the containment period, i.e., 1000 years after emplacement.

Repository designers can control the glass temperature to a certain extent by adjusting design parameters. Thus, another approach for identifying the plausible temperature range is to examine the temperature limits that have been established for design trade-off studies. This approach is based on the philosophy that design parameter combinations are acceptable if the design temperature limits are not exceeded. Although they could change in the future, values used in the past are instructive. For waste glass, these upper temperature limits have been 450°C for the time period when the glass is isolated from its surrounding environment by metal barriers and 150°C thereafter [CROFF-1986; JOHNSTONE-1982]. However, it is unlikely that design temperature limits exceeding the WAPS storage limit of 400°C (see Section 2.2.1) will be used in the future. The lower limits for temperature are set by the ambient temperatures in the possible host rock formations; these range from about 30°C for bedded salt to about 50°C for basalt [SRP-1986; BWIP-1987].

From the above discussion, the plausible limits for waste glass temperature in a saturated repository are <400°C before the hermetically sealed barriers are breached and 150 to 30°C subsequent to breaching (i.e., when the waste glass may interact with groundwater). The analytic results for the basalt and salt repositories indicate that the maximum temperatures are likely to be in the lower half of this range.

2.2.2.2 Pressure

In saturated host rock formations, the pressure of the groundwater that may interact with the glass (see Region 4 in Fig. 1-3) will be determined by hydrostatic, clay-swelling, and/or lithostatic forces. For host rock other than salt, the groundwater pressure will result from the combined hydrostatic pressure and the swelling pressure due to any confined swelling clay (bentonite) that may be used as a packing material. The hydrostatic pressure gradient is approximately 0.01 MPa/m of depth [DOE-1988b; DIXON-1986]. The maximum swelling pressure of confined bentonite packing is approximately 2.5 to 3.0 MPa [DIXON-1986]. Hence, assuming that the repository is located at a depth of 1000 m, the plausible range for groundwater pressure is 10 to 13 MPa.

For salt, the pressure of the groundwater that will interact with the waste glass is determined by the lithostatic pressure at the repository depth. The lithostatic pressure gradient is approximately 0.023 MPa/m [SRP-1986], which corresponds to a lithostatic pressure of 17.5 MPa for the target salt repository horizon (depth of 760 m) that was considered in the salt repository project. For salt repositories in general, the reasonably plausible range is approximately 15 to 20 MPa.

2.2.2.3 Hydrological Conditions

For a repository located in salt host rock formations, the evidence suggests that no brine movement occurs under ambient conditions [SRP-1987]. However, after waste emplacement, intergranular and intragranular fluids might accumulate at the location of an emplaced waste package; such accumulation could result from a pressure gradient flow in the laterally extensive microcracking that has been observed around excavated openings [LAPPIN-1989; BRUSH-1990] or from fluid inclusion migration up the temperature gradients. This accumulated brine represents a stagnant brine volume that could interact with the waste glass following breaching of the waste package containment barriers (i.e., Region 4 in Fig. 1-3 contains a stagnant brine volume).

Other less likely scenarios (including human intrusion through drilling) have been postulated that could allow brine to contact the emplaced waste in conceptually different modes involving some flow through or refreshment of the brine accumulated near the waste package. (Note: any intruding waters, e.g., from formations other than the host rock, would be expected to quickly become saturated with respect to dissolution of the host rock salt.) Because the ranges of flow or refreshment rates have not been determined, they have been treated, for testing purposes, as parameters that could span a wide range. The actual rates in a repository are most likely to be quite small.

In host rock formations other than salt, the excavated openings are expected to resaturate as a result of groundwater inflow from the surrounding host rock formation [DOE-1988b; CROFF-1986]. This accumulated groundwater, which is available to interact with the waste glass after the containment barriers are breached, is expected to be slowly refreshed as a result of flow due to pressure gradients and buoyancy forces [SEITZ-1986]. Other scenarios can be postulated that could involve significant flow or refreshment of the groundwater contacting the waste.

The plausible conceptual model for hydrological conditions with which the waste glass may interact is one in which the glass will be exposed to a stagnant or slowly refreshed groundwater volume. Because of uncertainties in possible ranges of flow or refreshment rates, the effects of flow and refreshment over a wide experimental range have been examined in waste glass corrosion tests (see Volume II, Section 2.3).

2.2.2.4 Geochemical Conditions

Important geochemical factors for the groundwater that may interact with waste glass include composition (e.g., silica content, anions, and cations), pH, and Eh. The plausible geochemical conditions for the groundwater with which the waste glass may interact span a broad range. The ambient conditions vary considerably between possible host formations and within individual formations [SRP-1987; BRUSH-1990; CROFF-1986; DOE-1988b]. The range of possibilities increases when the perturbations of waste emplacement are considered [SRP-1987; DOE-1988b].

To span the broad range of reasonably plausible conditions, the Materials Characterization Center (MCC) identified deionized water, a silicate groundwater, and brine (see Table 2-9) as reference leachants for testing purposes [PNL-1983; STRACHAN-1985]. For comparison, reference synthetic groundwater compositions that were established for testing purposes in the salt (Permian Basin brines [PBB]) and basalt repository programs are shown in Table 2-10. The PBB1 composition was intended to simulate a "dissolution brine" that would be expected to result from external fluids entering the host formation and becoming saturated as a result of dissolution of the rock salt in the host formation. This composition is similar to other reference compositions designed to simulate intrusion fluids [MOECKE-1983]. The PBB3 composition represents a fluid inclusion composition and was intended to simulate the brines that might contact emplaced waste as a result of fluid movement in the host formation. This composition is high in magnesium, as is the salt brine composition shown in Table 2-9. The composition of groundwater in other formations may be quite varied [CROFF-1986].

Table 2-9. Reference Leachant Compositions

Element	Silicate Water (mg/L)		Salt Brine (mg/L)	
	Detection Limit ^a	Concentration	Detection Limit	Concentration
B	0.01	0.04	0.1	17
Ca	0.01	--	0.1	302
Fe	0.005	--	0.05	0.3
K	0.3	--	300	26,800
Li	0.004	--	0.04	35.2
Mg	0.06	--	60	30,800
Na	0.01	47.9	10	34,400
Si	0.02	28.9	0.2	--
Sr	0.002	--	0.02	10

^aDetection limit in a solution with low ionic strength (from [STRACHAN-1985]).

Table 2-10. Reference Salt and Basalt Synthetic Groundwater Compositions

Species	Reference Brines ^a (mg/L)		Basalt Reference Groundwater GR-4 ^b (mg/L)
	PBB1	PBB3	
Na ⁺	127,000	25,470	334
Ca ²⁺	1,580	18,290	2.2
Mg ²⁺	132	59,310	0.0
K ⁺	40	10,690	13.8
Sr ²⁺	--	--	--
Zn ²⁺	--	--	--
Cl ⁻	191,300	238,480	405
Br ⁻	27	3,825	--
F ⁻	--	--	19.4
SO ₄ ²⁻	3,260	138	4.0
HCO ₃ ⁻	28	--	73.4
CO ₃ ²⁻	--	--	17.2
SiO ₂	--	--	96.1

^aFrom [SRP-1987].^bFrom [DOE-1988b].

Like composition, the pH and Eh of groundwaters can span a broad range and can be buffered to different extents. In general, however, the actual conditions in the groundwater that interacts with the waste glass will be determined by interactions with the engineered barrier materials and the waste glass. Waste glass corrosion is likely to control the pH in the immediate vicinity of the waste glass (i.e., Region 4 in Fig. 1-3) whereas the engineered barrier materials are likely to control the Eh.

2.2.3 Disposal Conditions in Unsaturated Geologic Settings

Unsaturated hydrologic environments are those above the water table where the rock pore space is not completely filled with groundwater. Following breaching of the containment barriers, the waste form in most of the breached waste packages is not expected to be in contact with liquid in these environments (i.e., Region 4 in Fig. 1-3 would not be filled with water); the expected fluid environment for the waste packages is an air/water-vapor mixture at a pressure of 0.1 MPa (1 bar). When the temperature is above the boiling point, the relative humidity will be low but will reach 100% when the rock porosity begins to saturate. Although unlikely, several scenarios are possible that may involve groundwater interacting with waste glass in unsaturated environments.

2.2.3.1 Unsaturated Hydrologic Conditions

Much of the current information relating to hydrologic conditions in deep unsaturated rock horizons has been generated as part of the Yucca Mountain Project [DOE-1990]. Two primary sources of information are the *Near-Field Environment Report* [WILDER-1992a, -1992b] and the *Site Characterization Plan* [DOE-1988a].

Both matrix and fracture flow can occur in unsaturated environments. Matrix flow refers to flow through bulk rock whereas fracture flow refers to flow through macroscopic fracture networks in the rock. Because Yucca Mountain tuff has small matrix pores, water is drawn into the pores by a very high capillary suction potential, causing the fractures to be drained of water under ambient conditions. The capillary suction potential is a barrier to the movement of water from the matrix pores into excavated or other openings. As long as rock around the waste package remains partially saturated and the capillary barrier is intact, only fracture flow will cause water to contact the waste glass.

Fracture flow can occur in response to a transient influx of water into the unsaturated zone, which may result from various sources ranging from a severe thunderstorm to a long-term episodic period of increased rainfall. In the unsaturated zone, the depth to which fracture flow persists below such a source of water is sensitive to interaction with matrix flow. Although unlikely, fracture-dominated flow is still the most likely source of water to contact the waste [BUSCHECK-1992]. Fracture-dominated flow occurs only under transient conditions when ponding remains at the fracture openings and is out of capillary equilibrium with the matrix. The amount of water contacting the waste packages would be limited both in quantity and contact time, even under the extreme conditions that would cause fracture flow to extend to the repository horizon depths.

After waste emplacement, thermal loading will drive moisture away from the waste packages [WILDER-1992a]. Initially, the large increase in vapor pressure will cause nearly all of the air to be driven away from the boiling zone, leaving the gas phase as nearly 100% water vapor. Heated vapor will be driven upwards from the thermal source toward a condensation zone where it will condense and drain through fractures. Because of the high permeabilities of the tuff stratigraphic units above the potential repository horizon, pressures in the vicinity of the waste packages will never be significantly above 0.1 MPa (1 bar). This means that for temperatures above 100°C, the relative humidity decreases rapidly with increasing temperature. Although the atmosphere will be oxidizing, the thermal effects of driving out ambient air and replacing it with water vapor will greatly lower the redox buffering capacity of the humid environment relative to air.

The plausible fluid environments for the waste packages will depend on design decisions to be made concerning the repository heat loading. The following discussion is intended only to illustrate some aspects of the plausible conditions that are relevant to glass corrosion. Although conditions will vary with the design of the engineered systems (in particular the thermal loading), the available results [WILDER-1992a] indicate that most waste packages will be exposed to a dry, low-humidity environment when the temperature is above ~100°C. However, for lower temperatures when the host rock begins to resaturate, the relative humidity will increase rapidly (see Fig. 2-4) and most of the waste packages will be exposed to a air/water vapor environment (i.e., Region 4 in Fig. 1-3 will contain humid air). Thus, even when the host rock is partially dried out, the relative humidity may be sufficient, at temperatures below ~100°C, to support measurable rates of glass weathering [ABRAJANO-1989].

Fig. 2-4. Relationship Between Percent Pore Saturation and Relative Humidity for Hydrologic Unit II-NL of Topopah Springs Tuff of 10% Porosity (believed to be equivalent to repository horizon). Surface forces between pore waters and rock surface effectively lower water activity from bulk water properties (adapted from [BRUTON-1992]).

Although it is unlikely, a possible scenario for glass-liquid water interaction in unsaturated environments is a case in which water, present in the fractures during an episode of fracture flow, drips onto the glass through a breached canister. Some of this water may pond for a period on the surface of the glass within the breached canister or it may trickle along the surface or through cracks in the glass before evaporating or exiting the canister through breach openings. From a glass corrosion perspective, these scenarios correspond to a partially water-filled canister (often referred to as a "bathtub" scenario) and a dripping water/humid air environment in Region 4 of Fig. 1-3 [APTED-1990]. Stoppage of the fracture flow episode will cause the ponded water to begin to evaporate, and the groundwater will become more concentrated with solutes and eventually precipitate salts corresponding to the salt components of the local groundwater. These components will be primarily sodium and calcium carbonates and sulfates plus silica (see Table 2-11 for compositions of local groundwaters at the Yucca Mountain site). Thus, even though the ambient groundwater has a low solids content, the groundwater contacting the waste could be quite saline for dripping scenarios (see Section 2.2.3.4 for further discussion of groundwater chemistry).

2.2.3.2 Temperature

Available calculations for the canistered waste package indicate that centerline temperatures may approach 200°C, and temperatures within a few meters of the waste package may remain above or at the local boiling point of water for several hundred years [BUSCHECK-1992]. However, because such results depend on several assumptions concerning waste package and repository design features, it may be better to assume that the plausible temperature range is established by the design temperature limits discussed in Section 2.2.2.1. In this case, the plausible range would be similar to that discussed for saturated conditions (Section 2.2.2.1).

2.2.3.3 Vapor Phase and Associated Radiation Effects

Because the total pressure (due to water vapor and air) cannot exceed 0.1 MPa (1 bar), the waste glass environment will have a low relative humidity until the temperature decreases to the boiling point. However, after the host rock begins to resaturate, when the temperature drops below the boiling point, the expected fluid environment for most of the waste packages is humid air. Under these conditions, the gamma radiation field produced by the waste packages has the potential to significantly alter the local redox chemistry and acidity of the small amounts of water that may interact with the waste glass. The radiation effects are more significant in air than in liquid water because of the presence of nitrogen in air and the acidic nitrogen radiolytic products that may be produced. For this reason, radiolysis is potentially more significant in unsaturated than saturated environments [VAN KONYNENBURG-1986].

The composition of the pre-emplacement pore gas in tuff has been well characterized as water-vapor-saturated air with up to 0.13 mole% carbon dioxide [THORSTENSON-1989]. The expected environment for most of the containment period is an air-water vapor mixture that would exist at temperatures from 27 to 250°C at a total pressure of about 0.1 MPa (1 bar). The key radiolytic products in this environment are (1) nitrogen fixation products: nitrogen acids, nitrogen oxides, and ammonia; (2) hydrogenous species: atomic and molecular hydrogen; and (3) oxygen-containing oxidizing species: oxy-radicals, ozone, and hydrogen peroxide. The key step in the formation of nitrogen oxides is the radiation-induced breakdown of molecular nitrogen to atomic nitrogen. In dry air and low-humidity systems, this breakdown leads primarily to the direct formation of nitrogen dioxide and nitrous oxide, along with trace concentrations of other oxides [VAN KONYNENBURG-1986]. Carbon dioxide is slowly decomposed to oxygen and carbon monoxide and could, therefore, undergo condensation reactions to generate organic compounds of higher molecular weight [REED-1992].

Radiolysis may result in a pronounced redox disequilibrium in a humid air atmosphere. It is expected to produce molecular hydrogen, ammonia, ozone, and hydrogen peroxide. Species such as hydrogen may diffuse out of the system and raise the overall oxidation state. Because of the presence of free oxygen in air and the radiolytic effects mentioned above, the environment in an unsaturated repository will be oxidizing.

2.2.3.4 Groundwater Chemistry

The chemical composition of pore water from the unsaturated (vadose) zone at Yucca Mountain is not known. However, the J-13 well water which originates from the Topopah Spring tuff is believed to be representative of the vadose zone pore water [WILDER-1992b]. The ambient conditions may be altered significantly by waste package emplacement. Increased temperatures in the

vicinity of the waste package will affect the local equilibrium between host rock and groundwater. Numerous experiments have demonstrated that the chemical composition of the water is controlled by the dissolution rates and solubilities of mineral phases present in the rocks [KNAUSS-1986a, -1986b, -1987]. As the water interacts with the rock, some minerals present in the rock will dissolve and new secondary minerals, including clays and zeolites, will form. The rates of the controlling dissolution and precipitation reactions are such that equilibrium will be approached on a scale of months to a few years. The particular assemblage that is stable will depend on the temperature and starting fluid chemistry.

Groundwater chemistries resulting from rock-water interactions at elevated temperatures are expected to be different for the near-field environment than for ambient conditions. Table 2-11 shows the fluid chemistry changes brought about by reacting J-13 well water, which originates from the Topopah Spring tuff at a depth below the water table, with Topopah Spring tuff at elevated temperatures [ABRAJANO-1988b; KNAUSS-1987]. The resulting concentrations of silicon are significantly higher, but other elements are not appreciably changed by hydrothermal reaction.

The effects of other repository materials must also be considered in evaluating glass corrosion and weathering under unsaturated conditions. Cements and grouts tend to increase the pH of fluids with which they react to values as high as 11.5 [MEIKE-1992]. Oxidation of metals present in the repository will lower the oxidation state of the groundwater by reacting with dissolved oxygen.

Table 2-11. Compositions of Groundwaters and Altered Groundwaters at the Yucca Mountain Site

Component	Concentration in Groundwater (ppm)			
	J-13 ^a	EJ-13 ^a	TST-90 ^b	TST-150 ^b
Al	0.012	<0.1	0.2	0.46
B	NA ^c	0.14	NA	NA
Ca	12.5	11.9	13.9	14.9
Fe	0.006	<0.01	NA	NA
K	5.11	NA	5.0	4.1
Li	0.042	0.046	NA	NA
Mg	1.92	0.95	1.31	0.092
Na	43.9	45.4	43.9	50.7
Si	27.0	30.6	47.2	141.6
Sr	0.035	0.043	NA	NA
U	NA	<0.001	NA	NA
F	2.2	2.45	2.2	2.2
Cl	6.9	7.70	7.4	7.5
HCO ₃ ⁻	125.3	NA	112.0	118.0
NO ₃ ⁻	9.6	8.35	9.1	9.1
NO ₂ ⁻	NA	<0.5	NA	NA
SO ₄ ⁼	18.7	18.6	20.6	20.7
pH	7.6	8.1	6.57	6.14

^aJ-13 refers to well water that originates from the Topopah Spring tuff at a depth below the water table; EJ-13 is J-13 water that was reacted with Topopah Spring tuff for 14 days at 90°C [ABRAJANO-1988b].

^bTST-90 and TST-150 refer to J-13 water that was reacted with Topopah Spring tuff at 90°C and 150°C, respectively, and 50 bars confining pressure for 304 days [KNAUSS-1987].

^cNA = not analyzed.

3.0 BOROSILICATE WASTE GLASS CORROSION

This section describes the important waste glass corrosion processes (Section 3.1), the controls on the rates of these processes (Section 3.2), and the quantitative modeling of waste glass corrosion and radionuclide release rates (Section 3.3).

3.1 Corrosion Processes

Experimental evidence for the important processes involved in aqueous corrosion and weathering of waste glass are summarized in Sections 3.1.1 and 3.1.2, respectively. More detailed information on the glass corrosion process is given in Volume II, Sections 2 and 3.

3.1.1 Aqueous Corrosion

Borosilicate glass corrosion in near-neutral to alkaline solutions is initiated through ion exchange and hydration of the glass by water. As discussed in Section 1.2.1, two primary processes take place, either of which is potentially rate controlling for the overall glass corrosion [WHITE-1986]: (1) diffusion of ions and water through the outer hydrolyzed layer of the dissolving glass and (2) dissolution of the glass network at the outermost surface of the reaction zone. Diffusion of ions is known to occur because of the observed diffusion profiles of ions in the outer hydrated glass layer and the nonstoichiometric release of ions in the early stages of leach tests [ABRAJANO-1987]. Network dissolution at the reaction zone-solution interface has been indicated by the observable migration of the surface layer boundary toward the fresh glass [LEE-1986a; ZOITOS-1991] and through mass balance calculations combined with surface analyses [ABRAJANO-1987].

With time, three types of layers develop on the glass surface, as shown in Fig. 1-1. Immediately adjacent to the fresh glass surface is the *diffusion layer* [ABRAJANO-1987], characterized by steep concentration gradients for alkali elements such as Na and Li. These elements undergo ion exchange for hydronium ions in solution through reactions such as reaction 1 in Table 1-1. Concentration data for ions are obtained from surface analytical methods such as secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy, and resonant nuclear reaction profiling [LANFORD-1979]. Typical concentration gradients for hydrogen, sodium, and calcium ions are shown in Fig. 3-1a [ABRAJANO-1987]. The complexity of the surface alteration layers that can be formed is illustrated by the SIMS data shown in Fig. 3-1b [WICKS-1993]. This figure shows a SIMS profile for the surface reaction layers formed on DWPF glass after two years of burial in the WIPP-MIT [WICKS-1993]. Although generally consistent with the schematic shown in Fig. 3-1a, it shows that the SIMS elemental profiles exhibit a rich variety of behavior. In fact, this behavior has been used to further classify the layer structure into two precipitated sublayers (designated α_0 and α_1), a gel layer (designated β_0), and a two-component reaction zone (designated by β_1 and β_2).

The water content of both the glass and glass alteration layers is determined by using either resonant nuclear reaction depth profiling [PHINNEY-1986] or Fourier transform infrared spectroscopy (FTIR) [AINES-1987]. Outward from the diffusion layer is a more hydrous layer of hydrated silica and alumina called the *gel layer*, which is often enriched in rare earths, some actinide elements, and divalent and trivalent cations such as Ca, Sr, Mg, and transition elements [WHITE-1986]. The cations enriched in this layer tend to be those that form the most insoluble oxide or silicate phases in the leach solution. In the gel layer, the tetrahedral network is broken down, and Si and elements other than the soluble alkali metals and B are released into solution; alkali elements and boron are released from the

Fig. 3-1a. Schematic Profile through Reacted Glass Layers, Including Concentration Profiles of Selected Elements Obtained Using SIMS (adapted from [BOURCIER-1990b]).

Fig. 3-1b. SIMS Profiles of SRS Simulated DWPF Glass After Two Years of Burial in the WIPP-MIIT Tests (adapted from [WICKS-1993]).

reaction zone before dissolution of the glass network. Diffusion gradients are not observed in the gel layer. The combined thickness of the gel layer and diffusion layer is commonly in the range of a few tenths of a micron to a few microns, depending mainly upon test duration, temperature, and pH. There is usually an outermost layer of secondary phases that may have initially precipitated or transformed in situ from hydrated gels into crystalline material. These precipitates may contain elements that originated in both the corroding glass and the contacting solution. This layer commonly is composed of clays, zeolites, and transition metal oxides (see Volume II, Section 2.1). Although there are reports in the literature of many more than three alteration layers on some glasses, these layers are usually composed of the gel and diffusion layers plus multiple layers of secondary phases.

Surface analytical methods have shown that the thickness of the diffusion layer remains nearly constant after an initial developmental period [ABRAJANO-1987]. Surface analysis suggests that glass corrosion occurring through network dissolution (in contrast to diffusion-controlled corrosion which occurs under acidic conditions) can be treated as a steady-state process where the diffusion layer of constant thickness migrates steadily into the fresh glass. Experimental evidence for this steady-state condition has been shown in diffusion profiles of reacted soda-lime glasses (Fig. 3-2) obtained through resonant nuclear reaction analysis [LANFORD-1979]. The hydrogen diffusion profile (represented by the portions of the curves in Fig. 3-2 that show a decreasing concentration with depth) remained unchanged for several hundred hours of reaction as the glass continued to dissolve, indicating that the diffusion layer thickness had reached a steady-state condition. Similar profiles have been obtained from reacted waste glasses [ABRAJANO-1987], but these profiles are not as clearly diagnostic because of the complexity introduced by the precipitation of thick layers of alteration phases on the glass surface or in-situ restructuring of the surface layers (see Volume II, Section 2.1).

Temperature affects dissolution behavior to different extents in a complex way [MAZER-1991], for example, by increasing the rates of surface reaction and diffusion [VERNAZ-1988; PETIT-1990a]. Typical activation energies for diffusion of water in glasses are about 80 kJ/mole [SMETS-1984] and are similar to those for surface dissolution reactions [KNAUSS-1990; WOOD-1983; MURPHY-1989], although, as shown in Section 2.1 of Volume II, considerable differences have been reported for different glass types [VERNAZ-1988]. There is, however, some evidence that formation of surface hydration layers is favored over dissolution in high-temperature corrosion tests [PETIT-1990a].

A continuous spectrum of behavior exists between (1) solids with fast surface dissolution rates relative to diffusion and (2) solids with slow surface dissolution rates relative to diffusion. Crystalline aluminosilicate phases leached in neutral to alkaline pH solutions fall into the first category; they seldom have thick reaction zones. However, bombardment by energetic ion beams serves to disrupt the crystallographic structure and increase diffusion rates through the surface layers [PETIT-1989]. When leached, these bombarded materials form thick diffusion layers much like those of waste glasses. Most waste glasses fall into the second category because their surface dissolution rates are slow relative to their diffusion rates.

When glasses are dissolved at constant pH [KNAUSS-1990], the dissolution rate as a function of pH appears as shown in Fig. 3-3. Rates are high at low and high pH values, and low at neutral pH values. Thus, in closed system tests (such as MCC-1), although the dissolution rate slows down, the rate coefficient (or forward reaction rate) is increasing as corrosion progresses due to pH increase associated with alkali release. However, the effect of decreasing chemical affinity for dissolution outweighs the effect of the increasing rate constant as the reaction proceeds (see Section 3.3.2.2).

Fig. 3-2. Resonant Nuclear Reaction Hydrogen Concentration Depth Profiles in Reacted Soda-Lime-Silica Glass as a Function of Time. Profiles at times 404 and 540 hours are nearly identical indicating steady-state dissolution conditions. Glass reacted in distilled water at 90°C (adapted from [LANFORD-1979]).

Fig. 3-3. Rate Constant for SRL 165 Simple Analog Glass (SRL-165SA) vs. pH at 25, 50, and 70°C Measured in Flow-Through Apparatus. Under these conditions, no secondary phases form and release rates are maximum values (adapted from [KNAUSS-1990]). SRL-165A glass composition is $\text{SiO}_2 = 55.7$, $\text{Al}_2\text{O}_3 = 11.7$, $\text{B}_2\text{O}_3 = 8.4$, $\text{Na}_2\text{O} = 18.2$, $\text{CaO} = 6.0$ wt. %.

Finally, properties of the leachate in the vicinity of the surface of the dissolving glass/gel layer are probably much different from bulk solution properties. Although difficult to document, it is likely that the fluid trapped inside the alteration rind of secondary phases has a chemistry that is controlled by the local environment (e.g., ion exchange with clays) and may not be well represented by bulk solution properties such as pH [BUNKER-1983]. This phenomenon could be important in predicting glass dissolution rates and has not been addressed in any current models.

3.1.2 Waste Glass Weathering

The corrosion of HLW glass in contact with aqueous solutions has been studied extensively, but relatively few studies have investigated the corrosion of waste glass under the range of conditions to which it might be exposed in an unsaturated repository (i.e., a repository where the excavated openings and fractures and pores in the host rock are not filled with water).

The following glass/water contact scenarios are possible in an unsaturated repository (see Section 2.2.3):

1. Water vapor contact with a continuous water film on the glass surface;
2. Periodic dripping in the trickle-through mode; and
3. Slow filling of a breached canister.

Corrosion of glass under these conditions is referred to as weathering. The key difference between these scenarios and the glass corrosion conditions discussed in previous sections is the limited volume of water available for reaction. Weathering that occurs as a result of static water in contact with the glass surface is referred to as "static weathering"; "dynamic weathering" is associated with moving water.

The reaction of HLW glass with water vapor has been examined in a series of studies at Argonne National Laboratory (ANL). Other studies have briefly exposed HLW glass to vapor [PICKERING-1980, YOKAYAMA-1985], but these were short-duration tests where only minor alteration was observed. The ANL work has examined the alteration of a series of HLW glasses, including (a) the DWPF-based compositions SRL 211, SRL 131, SRL 165, and SRL 202; (b) compositions WVCN 44, WVCN 50, ATM-10, and PNL 76-68; and (c) the French reference glass R7T7. Tests have been done at temperatures between 75 and 260°C, relative humidities of 0 to 100%, and times up to five years. During static weathering, it was observed that the glass generally altered to form a reacted layer and secondary precipitated phases [EBERT-1991b; BIWER-1990]. The reacted layer generally contains Fe- or Mg-rich clays with varying degrees of crystallinity. Segregation of actinide elements in calcium phosphate or titanium phases within the layer has also been observed [BATES-1992a, -1992b].

In a series of tests developed specifically to study the reaction of HLW glass when exposed to dynamic weathering, Bates et al. have contacted glass with controlled amounts of dripping water at 90°C [BATES-1985, -1986, -1990; WOODLAND-1991]. These tests have extended for long periods (six years) and have monitored the reacted glass surface, the release of glass components and actinide elements. In these tests spallation of the reacted layers has been reported as they form and undergo periodic wet-dry exposures. The layer for SRL 165 glass is essentially detached from the base glass [WOODLAND-1991]; during periodic flow, this layer is dislodged from the surface. Evidence for spallation has been observed for several test configurations [WOODLAND-1991], both in the solution analyses and in examination of the reacted glass surface.

Actinide concentrations in the leachates are controlled by several factors in these tests. Plutonium and americium have very low concentrations (10^{-10} to 10^{-12} M) in basic pH systems [EBERT-1990] and sorb strongly onto metal components in laboratory tests [BATES-1990; EBERT-1990; VERNAZ-1991]. Based solely on the dissolved fraction, for actinide-doped SRL 165 glass, Pu and Am normalized release was several hundred times less than the glass reaction, whereas Np and U release was almost congruent with the released glass components [BATES-1990].

From the information available on the weathering of commercial, historical, simple alkali silicate, natural, and HLW glasses (see Volume II, Section 3), static and dynamic weathering of waste glasses can be interpreted in terms of the processes already discussed for aqueous corrosion. Weathering observations include the initial formation of an alkali-depleted zone near the glass surface, with the alkali migrating to the surface and concentrating in the thin film of water on the surface. This initial process displays parabolic kinetics; however, over long periods of time or under accelerated test conditions, the corrosion rate can increase, resulting in thick reacted layers that form from the original surface of the glass inward. These layers are alkali depleted and exhibit some degree of crystallinity. This second-stage reaction appears to be linear with time. Abrajano

[ABRAJANO-1989] has suggested either ionic interdiffusion or molecular water diffusion as the rate-controlling step for the initial process that displays parabolic kinetics. If there is no process to remove alkali from the surface, then ion exchange is suppressed but water diffusion into the glass continues. When this happens, the glass structure remains intact but the water content of the glass is increased. If a sink is available for released alkali, either through incorporation into precipitated phases or through surface rinsing, the alkali-depletion process can continue. Concurrent with alkali depletion, hydrolysis reactions occur (see Table 1-1) and form a hydrolyzed surface layer that may exfoliate from the glass. Similar to aqueous corrosion, the dissolution reactions (i.e., reactions 6 and 7 in Table 1-1) may limit the rate of weathering during the second reaction stage. The crystallinity of the surface layers increases with time; secondary crystalline phases form on the glass surface as a result of restructuring of the amorphous layers formed initially. The formation of such crystalline secondary phases has been related to observed increases in the reaction rate. These increases have been explained by the onset of the formation of specific crystalline phases which results in a decrease in the solution concentration of elements that control the reaction affinity of the glass [EBERT-1991a].

In summary, the underlying processes controlling static and dynamic weathering are similar to those controlling aqueous corrosion. However, processes such as spallation of surface layers and colloid formation may be more important under weathering conditions (see Volume II, Section 2.6).

3.2 Controls on the Glass Corrosion Rate and Release Rates of Components

Although there is an extensive literature on glass dissolution testing (see Volume II, Sections 2 and 3), a few key experiments and observations are the most definitive for understanding the reactions and physical processes that control the rate of glass corrosion and the associated release of components into solution. Section 3.2.1 presents an overview of the experimental evidence that has provided insight into the processes and reaction steps controlling the corrosion rate. Controls on the release of components, including radioelements, are discussed in Section 3.2.2.

3.2.1 Corrosion Rate

Upon initial contact, water (as H_2O , H_3O^+ , or OH^-) diffuses into the glass and reacts with Si-O and Si-O-M bonds, preferentially at nonbridging oxygen sites [SMETS-1982], to form silanol groups ($\equiv Si-OH$). Cations such as Na^+ and Li^+ are released and diffuse out of the glass and enter the solution. Experiments show that boron is released at about the same rate as the alkalis. This is not expected if the structural configuration is important since most of the boron in the glass occupies four-coordinated sites similar to tetrahedral Si sites.

The alkali ions should be much more reactive and go into solution much faster than boron because they can be released in simple ion-exchange reactions, whereas boron-oxygen bonds must be hydrolyzed in order to release boron. Recent nuclear magnetic resonance (NMR) data for some alkali borosilicate glasses show that much of the boron in these glasses is clustered into alkali-boron rich zones [BUNKER-1990]. These zones would be much more susceptible to aqueous attack and would dissolve much faster than the silicate-rich zones surrounding them. This observation may explain the high rates of boron release observed for these types of glasses. Other elements (such as the actinides) can be released into solution only after hydrolysis of the framework Si-O bonds has taken place.

The commonly observed nonstoichiometric release of elements to solution is due to the incorporation of insoluble elements in either the altered surface layer or amorphous or secondary phase precipitates, and not to differential element mobilities in the surface layers. The lack of diffusion control of differential elemental release is consistent with corrosion studies and surface analysis of reacted borosilicate glasses. Experimental evidence suggests that the composition of the solution rather than the protective nature of the surface layers usually controls the corrosion rate (see Volume II, Section 2.1). Experiments where reacted glasses were removed from solution, and the solution was replaced with fresh distilled water, showed dissolution rates comparable to initial rates for PNL 76-68 glass [CHICK-1984]. If the surface layers provided a significant transport barrier that could affect the glass dissolution rate, then the rate after leachant change should have been slower than the rates observed. Conversely, in experiments where the reacted glass was removed from solution and replaced with fresh glass [CHICK-1984], the fresh glass dissolved at a much slower rate than the original glass, indicating that the rate is controlled primarily by solution chemistry and not by glass surface altered layers. The experimental evidence for evaluating the feedback effects of the growing surface layers and evolving leachate composition on glass corrosion is discussed more fully in Sections 2.1 and 2.3 of Volume II.

Additional evidence for the lack of control of reaction rate by transport through the alteration layers comes from leaching experiments of PNL 76-68 glass at a variety of S/V ratios [PEDERSON-1983]. Reaction layer thicknesses were measured using SIMS. Although the leached layers were much thicker in the low S/V tests, the leach rates were identical when normalized by their S/V ratio. Control of release rates by diffusion through the surface layers is not consistent with this observation. Again, solution composition, and in particular dissolved silica concentration (see Fig. 3-4) [PEDERSON-1983; LANZA-1988], appeared to be the dominant control on glass dissolution rates (see Volume II, Section 2.3, for a more complete discussion).

Further evidence comes from experiments with PNL 76-68 and C31-3 glasses where the surface layers were physically removed from the glass surface and the samples then replaced into the same test vessel [GRAMBOW-1984b]. The release rates were relatively unchanged, again indicating the lack of control by transport through the surface layers (see Volume II, Section 2.1.3).

Investigations with analytical electron microscopy (AEM) [ABRAJANO-1990; LUTZE-1988b] are consistent with the lack of transport control of the glass dissolution rate. The studies show that the layers of amorphous and crystalline secondary phases do not appear to provide a diffusion barrier that controls the reaction rate. The surface layers appear to contain numerous channelways for transport of aqueous species; these layers readily flake off reacted glass samples, indicating that they do not provide a coherent transport barrier over the glass surface. There is, however, evidence that the surface layers can be protective under some circumstances, particularly under alkaline conditions and in MgCl_2 -rich solutions such as sea water [MALOW-1982; ZOITOS-1988] (see Volume II, Section 2.1.3).

Raman and nuclear magnetic resonance spectroscopic studies of alkali borosilicate glasses show that there is extensive condensation (i.e., repolymerization) of the silicate structure following water hydrolysis [BUNKER-1988]. After Si-O bonds are hydrolyzed to form silanols and cations are released from the glass, the structure quickly reforms through condensation of the silanols, as evidenced by the fact that ^{17}O doped into the leachant occurs later in Si- ^{17}O groups in the gel layer. During leaching, the hydrolyzed glass network apparently opens up, releases metals, and repolymerizes to form a more stable hydrous gel. This gel continues to react with water at the water-gel boundary to dissolve completely into monomeric silicic acid. During this hydrolysis process, all cations not

Fig. 3-4. Boron Release after 28 Days of Leaching of PNL 76-68 Glass at 90°C in Solutions of Varying Initial Silica Concentrations (X-Axis) (adapted from [PEDERSON-1983]).

incorporated into the condensed gel structure are free to diffuse out into solution. Based on the corrosion behavior of several sodium borosilicate glasses characterized using depth profiling and ^{11}B nuclear magnetic resonance (NMR), Bunker [BUNKER-1986] concluded that, in most environments, network hydrolysis controls the kinetics of glass corrosion.

Pederson provided further evidence for surface reaction control, rather than transport or diffusion control, in studies of leaching rates of sodium silicate glasses in D_2O solutions [PEDERSON-1987]. Changes in glass dissolution rates caused by substitution of D for H, and ^{18}O for O, can be used to infer rate-controlling mechanisms. Mass differences will affect, to different extents, reaction rates limited by diffusion or reaction at a bond site. Pederson explained the lower rates of reaction in D_2O , compared to H_2O , as being due to a rate-limiting hydrolysis step in the corrosion of the silicate matrix [PEDERSON-1987]. The study also showed no change in isotope effect during several hours of reaction (see Fig. 3-5), and there appeared to be no change in the rate-controlling mechanism during the transition from parabolic to linear kinetic behavior. If the rate-limiting reaction had changed during the transition from diffusion control to surface reaction control, a corresponding shift should occur in isotope effect. However, as shown in Fig. 3-5, such a shift in the isotope effect was not observed; the reaction rate apparently was controlled at all times by a hydrolysis step [PEDERSON-1987]. This result is consistent with the hypothesis that a network hydrolysis step controls the rate of both the diffusion-limited ion exchange (suggesting that water diffusion by a hydrolysis mechanism controls the rate of ion exchange) and dissolution-limited corrosion processes.

Fig. 3-5. Plot of Extent of Reaction (H^+ -Consumption) vs. Time for Sodium Silicate Glass Reacted in HCl Solution at Constant pH in Both H_2O and D_2O Solutions. Constant difference in rate with time indicates a constant rate control mechanism throughout time interval of experiment, in spite of trend showing early parabolic behavior becoming linear with time (adapted from [PEDERSON-1987]).

More recent isotopic data [PEDERSON-1990] for more durable (Na-Al-Si) glasses showed evidence for transport control of reaction rate during early reaction times, before buildup of silica and other glass components in solution. Transport control is through diffusion of water or some other H-containing species. Some evidence also exists that transport control through the surface layers may become rate limiting at longer times under some conditions (see Volume II, Section 2.1.3).

In summary, a surface dissolution reaction apparently controls the overall corrosion rate of HLW glasses under many test conditions. This hypothesis is consistent with most observations of HLW glass corrosion tests under neutral to alkaline pH conditions. In particular, it explains the observation of an "affinity effect" in corrosion rates where the corrosion rates decrease as the concentration of silica increases in solution. It is the buildup of species in solution that serves to "saturate" the solution with respect to the dissolving glass, thereby decreasing the corrosion rate. This buildup and the effects on the corrosion rate explain the observed S/V effects discussed in Volume II, Section 2.3. In flow-through tests where there is no buildup of species in solution and where protective layers do not form on the glass surface [KNAUSS-1990], the limiting rate is constant with time. In tests where the leachant is doped with silica, the rate of dissolution decreases drastically, as illustrated in Fig. 3-4 [GRAMBOW-1987a; PEDERSON-1983]. Even the rate of release to solution of boron, an element not approaching saturation with respect to any boron phase, decreases in experiments where the leachant is enriched in silica [PEDERSON-1983]. This indicates that the release rates of all components of the glass, regardless of solubility characteristics, are decreased uniformly by the affinity effect.

Most studies directed at the effects of glass composition on glass corrosion rate have not clearly separated the effects of glass composition from those of other parameters. For example, the multitude of leach tests on waste glasses of a wide variety of compositions in MCC-1 and MCC-3 experiments [MCC-1985] are not optimum for this purpose. Although relative durabilities can be determined for the specific test conditions, the compositional effect cannot be clearly separated from the effect of differing solution chemistry as the tests proceed. Test results of this type cannot be used directly to quantify the effects of glass composition on glass corrosion rate.

For example, if two glasses with significantly different alkali contents are leached in distilled water, the glass with the higher alkali content will rapidly ion exchange and raise the pH of the solution to a higher value than the alkali-poor glass. Because the intrinsic rate of reaction increases with increasing pH under alkaline conditions (see Fig. 3-3), the rate of glass corrosion will increase. Thus, the corrosion rates of the two glasses will be compared under conditions where the differing solution compositions also have an effect on glass corrosion rate that cannot be separated from the glass compositional effect.

A few studies, where the compositional effect is clearly isolated, show that this effect on dissolution rate is complex. Adding Al to alkali silicate glasses [SMETS-1982] increases glass durability by causing Na^+ ions to be located adjacent to Al^{3+} ions to balance charge (note: charge balance or charge compensation is required when trivalent network-forming components such as Al^{3+} , B^{3+} , or Fe^{3+} are included in the glass network in place of tetravalent silicon) rather than being located at nonbridging oxygen sites in the glass structure. This shift decreases the diffusion rate of water through the structure, which also enhances durability. It has also been shown that addition of alumina to glasses can inhibit surface swelling and thereby decrease transport rates [DOREMUS-1983b]. On the other hand, it has been reported that Al may promote precipitation of secondary aluminum silicate phases (such as analcime) which lowers the silicic acid concentration in solution and thereby increases the corrosion rate [VAN ISEGHEM-1988]. These results indicate that while Al may increase

durability during Stage 1, it may increase the corrosion rate during Stage 2. The effects of alkaline earth ions on glass corrosion are particularly complex [ISARD-1986] and may increase or decrease the durability, depending on pH and the cation added. Trotignon [TROTIGNON-1991] looked at the dissolution behavior of a range of systematically more complex borosilicate glass compositions with complex results (see Volume II, Section 2.2).

Some closed-system leach tests of powdered glasses [FENG-1989b; KINOSHITA-1991] have shown that relatively small compositional differences can give rise to large differences in glass durability. A large increase in durability was observed when 2 to 3 wt.% of silica was added to a base WV205 glass composition; this effect is explained in terms of the influence of the added components on the glass structure [FENG-1989b]. The types and amounts of metal oxides added to the borosilicate framework of waste glasses will affect the structure and may change transport rates (e.g., water diffusion) through the glass, which in turn can affect corrosion rates.

Data for a variety of Swedish glass compositions have been reported by Clark et al. [CLARK-1987]. The glasses were ranked by both release rates to solution and the depth of water penetration by SIMS analysis, and approximately the same durability order was found using both criteria. The relationship between composition and durability was complex. Additional data for several waste glasses reacted in pulsed-flow experiments have been reported by Barkatt et al. [BARKATT-1987] which show the importance of the effects of the alkali components of the glass on the pH of the leach solution and the glass corrosion rate.

The hydration theory for determining glass durabilities [PAUL-1977, -1982; PLODINEC-1984; JANTZEN-1991] has been used to correlate glass durability with an estimated free energy of hydration of glass. The thermodynamic properties of the glass were approximated by a mixture of simple oxides and silicates summing to the bulk composition of the glass. These studies showed a gross correlation between short-term glass corrosion rates and hydration free energy [PLODINEC-1984; JANTZEN-1984b, -1986b]. However, hydration theory alone is unable to predict the relative durabilities of borosilicate glasses [BUNKER-1987] and other simple glasses [PERERA-1991]. Empirical regression models of glass composition vs. durability can provide better correlations with experimental data than hydration theory [ABRAJANO-1988a] (see Volume II, Section 2.2.5, for further discussion of the application of hydration theory to examination of compositional effects on corrosion).

An additional problem in relating glass composition to glass durability is that the relative durability of glasses in short-term experiments may not correlate with their long-term dissolution behavior. For example, SRL 165 glass was found to be more durable than PNL 76-68 glass when reacted in water, but the reverse was true in weathering tests where the glasses were reacted in water vapor [ABRAJANO-1989]. Weathering tests in humid environments have very high effective S/V ratios and are used as indicators of long-term behavior because they accelerate reaction progress. Apparently, the composition of SRL 165 glass is more amenable to forming stable secondary phases that precipitate on the glass surface, keeping the solution concentrations of silica and other species low and, as a result, increase the corrosion rate. The PNL 76-68 glass tends not to form such secondary phases in vapor hydration tests and, therefore, reacts more slowly than the SRL 165 glass in such tests. Similar problems may arise in trying to relate short-term glass corrosion tests in water to long-term corrosion in a repository under episodically saturated and unsaturated environments.

The effects of glass composition on glass corrosion under repository conditions is a complex issue. Such effects are difficult to isolate and quantify without carefully designed experiments. Also, understanding these effects depends on knowing what the rate-limiting reaction mechanism is and how it may change with both composition and environmental conditions.

3.2.2 Release Rates of Components

The release of components (including radioelements) from HLW borosilicate glass into contacting water is constrained by the corrosion rate of the glass, by dissolution of the insoluble components, and by coprecipitation with and adsorption onto secondary phases, e.g., the secondary phases that constitute the gel and precipitated layers. A more complete discussion of these controls is provided in Volume II, Section 2.7.

Typical release trends for soluble elements in closed-system tests show a parabolic trend, that is, an initial high release rate (note that the release rate is the time derivative of the cumulative release curve) that decreases and becomes approximately linear with time (Fig. 3-6). This has often been used as evidence for diffusion control of the reaction rate. Although initial rapid ion exchange and associated diffusion of ions and water through a continuously forming diffusion layer may be responsible for the early parabolic behavior [WHITE-1986], later corrosion behavior is usually controlled by the rate of surface dissolution. Regression of equations describing the two types of rate control (i.e., surface layer diffusion and dissolution reaction) were made on the data shown in Fig. 3-6. The results indicate that such data are explained equally well by assuming reaction affinity or surface layer diffusion control for the release rate [BOURCIER-1991]. For most glasses, the initial rate-limiting process is diffusion; after a few hours to weeks (depending on test conditions), this changes to surface reaction control. Figure 3-6 indicates that resolving this changeover is difficult and that curve fitting of observed leaching trends alone is not conclusive for distinguishing between the two mechanisms; additional information is needed (see Section 3.2.1).

The change in pH with time during leach tests reflects the complexity of the corrosion process. In leach tests of simulated waste glasses with J-13 well water, ion exchange of H_3O^+ in solution for alkalis in the glass initially causes the pH to rise. Dissolution of the alkali and alkaline earth components of the glass also causes the pH to increase due to reactions such as

Amphoteric components such as alumina will, under basic conditions, lower the pH through the reaction:

Fig. 3-6. Silica Release Data for SRL 165 Glass Reacted at 150°C in 0.003 M NaHCO₃ Solution (solid points). Curves are regressed to the data using equations for diffusion control (rate = $A + Bt^{1/2}$ and affinity control (rate = $Ak_+(1 - Q/K)$) for reaction rate. Both models fit the data to within experimental error (adapted ([BOURCIER-1991])).

Under acidic conditions dissolution of alumina from the glass will increase the solution pH. Precipitation of secondary phases also affects the pH of the solution, depending on whether the precipitation reaction consumes or releases acid. These dissolution and precipitation processes give rise to a complex change of pH with time for unbuffered glass-water systems. Usually, the pH rises steadily throughout the reaction, rising more quickly at first and gradually slowing and leveling off with time.

The changes in aqueous solution concentrations of other ions are also highly variable. Concentrations of elements such as B and Li, which are not concentrated in the gel layer or precipitated as secondary phases during the early stages of glass corrosion, increase with time as the glass corrodes. Boron and Li release rates are usually rapid at first, and then slow down with time. Concentrations of elements such as Ca and Mg, which are concentrated in the gel layer and which may precipitate in secondary phases such as clays and carbonates, may remain steady or decrease as a complex function of time. Although the release rates of insoluble elements are controlled by coprecipitation, adsorption, and other solubility constraints, no simple rules govern the release behavior of specific elements. The release of sparingly soluble elements can only be understood with the

application of models which include provisions for all processes affecting element solubilities (see Volume II, Section 2.7). They vary with the type of glass, the type of reactant solution, the pH, redox conditions, and temperature of the experiment.

Many of the metals associated with the corroding glass do not go into solution as the gel layer is formed. Analytical electron microscopy investigations of the surface layers of reacted HLW glasses [ABRAJANO-1990; PETIT-1990a] indicate that the glasses form surface layers composed of such phases as di- and tri-octahedral smectites, serpentines, and transition metal oxides and silicates. Commonly, the initial phases formed are amorphous hydrosilicates that, with time, segregate into distinct crystalline phases. This segregation is consistent with analyses of leachates in glass corrosion tests in which the relatively insoluble elements (i.e., Al, Fe, Mn, and Ca) are released more slowly and do not build up in solution as do the soluble elements (i.e., B, Na, and Li). The insoluble radioelements, which are present as minor components, are often coprecipitated with or adsorbed onto these secondary phases.

However, even sparingly soluble elements that have slow release rates may diffuse readily through the alteration layers. Greaves [GREAVES-1990] examined Fe- and U-containing alkali borosilicate glasses with the glancing-angle X-ray absorption fine structure (EXAFS) technique. The EXAFS technique can be used to characterize the outermost few hundred angstroms of glass surface layer in terms of elemental composition, bond length, and coordination. Greaves found that along with Na, both U and Fe readily diffuse to the glass surface where the Fe precipitates as octahedrally coordinated oxide or silicate phases and U precipitates as a uranyl silicate; Na is released to solution. Experimental results for the release of individual radioelements and the forms in which they are released to solution (i.e., as solutes and colloids) are discussed in Volume II, Section 2.7. Modeling considerations are discussed in Section 3.3.2.2.

3.3 Modeling of Glass Corrosion Rate and Associated Radionuclide Release Rates

The long history of glass/water reaction studies has led to the collection of a massive amount of corrosion data on all types of glass compositions. Experiments alone are insufficient to predict waste glass corrosion because they cannot be performed over time periods as long as the tens of thousands of years over which the radionuclides will be released, and they cannot be performed for the numerous sets of possible conditions anticipated for candidate repositories. In addition, successful extrapolation of experimental data to conditions outside the range of what can be measured demands an understanding of the complex chemical and physical processes taking place. Also, a mechanistic chemical model for glass corrosion is necessary in order to couple waste glass corrosion with the behavior of other repository materials also undergoing degradation by reaction with groundwater. All of these reactions are coupled by the action of a common reservoir of water interacting with each type of repository material (see Fig. 1-3). Although identification of the important chemical processes taking place during glass dissolution is best achieved through carefully designed experiments, an understanding of the interactions and coupling of these processes is best achieved through modeling combined with experiment.

The goal of chemical modeling of the reaction of HLW glass with water is to make credible long-term predictions (10,000 years or longer) of the rates of glass degradation and the associated radionuclide releases in a repository environment. To make defensible predictions of long-term alteration, the model must be based on a mechanistic understanding of glass corrosion; simple

extrapolations of short-term test results according to an empirical rule are not sufficient. Many of the approaches to the problem of predicting long-term glass corrosion rates are discussed in Sections 3.3.1 and 3.3.2.

3.3.1 General Overview

The consensus among most researchers is that the glass corrosion rates observed in laboratory experiments are controlled primarily by the silica concentration in solution [ADVOCAT-1990; PEDERSON-1983; VAN ISEGHEM-1988; CURTI-1991; VERNAZ-1992; GRAMBOW-1987a]. However, other dissolved species also affect glass corrosion rates [BUCKWALTER-1982; McVAY-1983; MENDEL-1984; LEHMAN-1985; LEE-1986b; FENG-1987]. The uncertainty that remains centers on whether dissolved species affect the reaction rate through surface complexation, precipitation of secondary phases, saturation effects (see below), or a combination of effects.

Most modeling efforts to date have been applied to the glass corrosion rate; they have not dealt explicitly with the release rates of radionuclides from the glass waste form. The integrated rate of glass corrosion provides a conservative upper bound on the integrated rate of release of radionuclides; that is, the cumulative release of radionuclides from the glass cannot exceed the amount associated with the portion of the glass that has corroded. In fact, as discussed in Volume II, Sections 2.7 and 3.6, only a small fraction of most of the radioelements associated with the corroded glass are released as solutes and colloids. Although there are numerous experimental studies of the release rates of radionuclides from waste forms [BRADLEY-1979; FILLET-1985; SCHRAMKE-1985; VERNAZ-1991; GRAMBOW-1991a], including comparisons with actinide solubilities of discrete phases [KERRISK-1985b; WILSON-1991], few attempts have been made to incorporate these results into mechanistic models of glass corrosion. For mechanistic modeling, better quantified information is needed, especially in the areas of (1) solubilities of actinides as trace and minor components in the commonly formed clay, zeolite, and oxide alteration phases; (2) stabilities and formation rates of colloids; (3) stabilities of actinide complexes; and (4) the sorption behavior of radionuclides onto mineral surfaces, including both colloids and alteration phases. Current geochemical computer codes used to model glass dissolution are being enhanced to include these chemical processes. Both better and more quantitative experimental data and computer code enhancements are needed to enable quantitative predictions of specific radionuclide release rates from the glass waste form. For many important radionuclides, however, this refinement of modeling capability may not be necessary; constraints based only on glass corrosion rates may suffice. The focus here is, therefore, on approaches for modeling the glass corrosion rate.

3.3.2 Approaches to Modeling Glass Corrosion Rate

Most experimental evidence suggests that the waste glass corrosion rate is controlled by dissolution, with surface layer diffusion controls being important under some conditions (see Section 3.2.1). Models based on diffusion mass transport control are discussed in Section 3.3.2.1, and models based on dissolution and dissolution plus diffusion control are discussed in Section 3.3.2.2.

3.3.2.1 Models Based on Diffusion Control

One category of mass transport models involves the solution of diffusion equations for a moving boundary layer, where the rate of reaction is controlled by water diffusion [DOREMUS-1983a; HARVEY-1986a, -1986b, -1987, -1989] or by diffusion of other species involved in the ion-exchange process [DOREMUS-1975; ISARD-1982; SMETS-1983; CONRADT-1984]. This approach has its

origins in studies of dissolution of simple glasses over short time periods where reaction rates are diffusion-limited and rates are not affected by saturation effects (i.e., the models focus on Stage 1 of glass corrosion discussed in Section 1.2.2). However, the dissolution rates of typical HLW glasses were not well reproduced and were termed "anomalous." Another approach combines rate control by transport or ion exchange with a term to account for the effect of a growing surface layer that provides a diffusion barrier for subsequent reaction [WALLACE-1983; MURAKAMI-1984; BANBA-1985, -1987]. Still other approaches are various combinations of the above processes, which account for flow conditions and glass saturation effects as well [MACHIELS-1981; PESCATORE-1982; HARVEY-1984; CONRADT-1985]. Modeling the effects of mass transport through surface layers in waste glass corrosion is discussed in Section 3.3.2.2.1.

3.3.2.2 Models Based on Dissolution Control

Although diffusion-controlled mass transport models may be applicable to some glass compositions, definitive experiments showed that glass dissolution rates for more durable borosilicate waste glasses are essentially independent of alteration layer thickness [PEDERSON-1983; CHICK-1984]. The alteration layers usually do not provide a rate-limiting transport barrier to control the reaction rate (see Volume II, Section 2.1.3). Glass corrosion rates are usually controlled almost entirely by solution composition, in particular, dissolved silica concentration and pH. The evidence for surface layer effects in some experiments has led to the development of models based on combined diffusion and dissolution control.

The approach most widely used to model borosilicate waste glass corrosion assumes a surface dissolution reaction control for the corrosion process and explicitly accounts for the formation of alteration and secondary phases, with feedback from the evolving solution composition. The reaction path is calculated to track this feedback and to determine the effects on the corrosion rate. Although diffusion takes place, it is assumed not to be rate limiting and is, therefore, not explicitly included in some models. Modeling has also been performed with reaction path modeling codes such as EQ3/6 [WOLERY-1979], PHREEQE [PARKHURST-1980], and SOLMNEQ [KHARAKA-1973]; but without explicit provision for glass dissolution kinetics [STRACHAN-1984; SAVAGE-1986; BRUTON-1988; EBERT-1992]. In these modeling simulations, glass is reacted with an aqueous solution at an arbitrary rate and mineral precipitation/dissolution reactions are evaluated during the reaction. The results give the predicted solubility-limited concentrations for elements that form relatively insoluble secondary phases, such as all of the actinides.

The two primary features of glass corrosion that must be taken into account in modeling glass corrosion kinetics are (1) the change in reaction rate with time and (2) the nonstoichiometric release of elements to solution (Fig. 3-7). The primary reason for nonstoichiometric release is the precipitation of secondary phases; these phases selectively incorporate the less-soluble glass components, which therefore, do not show up in solution analyses. The basis of the reaction path model (such as PHREEQE or EQ3/6) is shown in Fig. 3-8. The glass begins to react through ion exchange and hydration. A steady state is quickly reached in which the alteration layer maintains a nearly constant thickness and network dissolution controls the overall corrosion rate. After this steady state is established, the diffusion-controlled ion-exchange process continues, but its rate is controlled by the rate of the dissolution process (see Section 1.2.2). Glass dissolution is stoichiometric from this point on, but measured concentrations of elements in solution do not appear to be stoichiometric, but instead

Fig. 3-7. Typical Normalized Element Release Profiles for SRL-165SA Glass Reacted at 150°C in 0.003 M NaHCO₃ Solution with S/V = 0.01 cm⁻¹. Less-soluble elements are incorporated into secondary phases and show reduced release rates (adapted from [BOURCIER-1990b]).

reflect the fact that precipitation of secondary phases affects some elements more than others. The reaction path codes are used to compute the aqueous solution speciation and mineral saturation states. Supersaturated phases are allowed to precipitate and maintain equilibrium between aqueous solution and precipitating solids.

Because the glass network dissolution involves network hydrolysis reactions (see Table 1-1), the dissolution rate of glass is calculated using a reaction path model in conjunction with the following rate equation, which is based on macroscopic irreversible thermodynamics [AAGAARD-1982] applied to hydrolysis reactions:

$$\frac{dn_i}{dt} = S v k_f (a_{H^+})^h (1 - e^{-A/RT}) \quad (5)$$

Fig. 3-8.

Schematic Illustration of the Evolution of Surface Layers on Reacting Glass. This conceptual model is the basis for the steady-state assumption in reaction path models for glass dissolution.

where n_i is the number of moles of specie i in solution, S is surface area (cm^2), ν is the stoichiometric factor, k_f is the forward rate constant ($\text{mole}/\text{cm}^2/\text{s}$), a_{H^+} is the activity of hydrogen ions, A is the dissolution affinity (kcal/mole), R is the gas constant ($\text{kcal}/\text{mole}\cdot\text{K}$), and T is the absolute temperature (Kelvin). Affinity is defined as $A = -RT \ln(Q/K)$, where Q is the activity product of aqueous species involved in the dissolution reaction for the dissolving solid and K is the equilibrium constant for that same solid. The term $(1 - e^{-A/RT})$ in Eq. 5 can therefore be rearranged to $(1 - Q/K)$. Equation 5 can be derived by starting with the general rate equation [LASAGA-1984]

$$\frac{dc_i}{dt} = \frac{S}{V} \nu k_f (a_{H^+})^h + \frac{S}{V} \nu k_r (a_{H^+})^h \quad (6)$$

where c_i is the concentration of specie i in solution, V is the solution volume, k_f is the forward rate constant (dissolution), and k_r is the backward rate constant (condensation). The principle of detailed balancing states that the net rate of a reaction is the difference between the rates of the forward and reverse reactions. At equilibrium, the rates are equal and

$$K = \frac{k_f}{k_r} \quad (7)$$

Equation 5 is derived by assuming that the principle of detailed balancing holds and that the driving force for a reaction is proportional to the extent of disequilibrium, or affinity, of the reaction. The farther from equilibrium, the stronger is the driving force. The affinity term accounts for the effect of increasing the concentrations of species in solution, in particular silica, on the rate of dissolution.

Equation 5 describes the rate of dissolution reactions at the glass surface. In high pH solutions, the rate-controlling reaction probably involves hydrolysis of surface Si-O bonds by hydroxide ions (see reaction 6 in Table 1-1):

At neutral pH, where hydroxide ions are much less abundant, the reactant is most likely water (see reaction 7 in Table 1-1):

At acidic pH, electrophilic attack is by the hydronium ion (H_3O^+).

The v-shaped dependence of the log of the glass reaction rate on pH (Fig. 3-3) may be explained in terms of these reactions. At low and high pH, the glass structure is actively hydrolyzed by H_3O^+ and OH^- . At neutral pH, where H_2O is the dominant reacting species, rates are lower because of the slower rate of attack by uncharged water relative to charged OH^- and H_3O^+ species. Different glass compositions react at different rates, presumably because of different bond angles and coordination of Si-O groups and cations on the glass surface.

Equation 5 has been used to model the dissolution kinetics of aluminosilicate phases [AAGAARD-1982; MURPHY-1989] and some synthetic silicate glasses [MAZER-1987]. This rate equation predicts that the dissolution rate, as determined by the rate of change of concentration of a leached component, e.g., boron, will be a function of the S/V ratio (a factor common to most rate expressions), a pH-dependent rate constant, and an affinity term (which decreases as the system approaches equilibrium).

The various glass corrosion models incorporate Eq. 5 to determine the rate at which glass dissolves into solution. Because the affinity term changes with reaction progress, it is necessary to determine the reaction path. Glass corrosion rate models, therefore, incorporate the dissolution rate equation (i.e., Eq. 5) into a general reaction path program that provides for aqueous speciation and precipitation of secondary phases as the solutions become saturated. Thus, the models account for both the rate-limiting reaction that controls dissolution and the effects of surface layer formation on solution chemistry. Glass is allowed to dissolve stoichiometrically into solution at the rate determined

by the rate of dissolution. Nonstoichiometric release is accounted for by the incorporation of elements into secondary phases and by amorphous precipitates. Specific models that have implemented this general approach for nuclear waste glass corrosion are discussed below.

3.3.2.2.1 Grambow Model

The borosilicate glass corrosion model of Grambow is the most highly developed and widely used [GRAMBOW-1984a, -1985, -1987a, -1988a, -1988b]. The model has evolved and improved with time. It is based on Eq. 5 to describe the rate of the dissolution step and is simplified to include only the concentration of silica in the affinity term. That is, the reaction affinity for glass dissolution is calculated using only the activity of dissolved silica as the value for Q , and K corresponds to a silica "saturation" value for a particular glass composition at some temperature and pH. Thus,

$$R_M = \frac{1}{S} \frac{d[H_4SiO_4]}{dt} = k_+ \left(1 - \frac{[H_4SiO_4]_s}{[H_4SiO_4]_{sat}} \right) \quad (10)$$

where R_M is the rate of matrix dissolution (mole/cm²/sec), $k_+ = k_f(a_{H^+})^h$, $[H_4SiO_4]_s$ is the activity of aqueous silica at the reacting surface, and $[H_4SiO_4]_{sat}$ is the silica activity at saturation. The parameters k_+ and $[H_4SiO_4]_{sat}$ are regressed from experimental data, and may vary with glass composition, solution composition, and temperature. The model does not provide for any dependence of k_+ on pH. As yet, no methodology is available to adjust these parameters for glasses or test conditions differing from those from which the parameters were regressed.

The Grambow model also includes a transport term for the diffusion rate of aqueous silica through a hydrous surface layer (gel layer) on the glass. Some flow-through glass corrosion tests exhibit a maximum in dissolution rate after a few days, which can be explained as resulting from the formation of a surface layer that limits the rate of dissolved silica transport and thereby controls the overall rate of glass dissolution. The rate equation that Grambow uses to describe transport control through silica diffusion is

$$R_T = \frac{D}{L} ([H_4SiO_4]_s - [H_4SiO_4]) + R_\infty \quad (11)$$

where R_T is the transport-limited glass dissolution rate; $[H_4SiO_4]_s$ and $[H_4SiO_4]$ refer to silica activities at the gel layer-glass interface and in bulk solution, respectively; D is the diffusion coefficient for silica in the surface layer; L is the alteration layer thickness; and R_∞ is the long-term rate for glass corrosion under silica saturation conditions.

At steady state, the silicic acid concentration at the interface between the reaction zone and gel layer does not change with time and hence the rate of mass transport (R_T) is equal to the rate of matrix dissolution (R_M). Hence, when R_M is equated to R_T and the resulting equation solved for $[H_4SiO_4]_s$, which is then substituted into Eq. 10, one obtains the master rate equation for the Grambow model [GRAMBOW-1992]:

$$\frac{1}{S} \frac{d[H_4SiO_4]}{dt} = k_+ \left(\frac{(D/L)([H_4SiO_4]_{sat} - [H_4SiO_4]) + R_{\infty}}{(D/L)[H_4SiO_4]_{sat} + k_+} \right) \quad (12)$$

These rate equations are embodied in the computer code GLASSOL. Aqueous speciation and mineral saturation states are provided by the interface of GLASSOL to the program PHREEQE [PARKHURST-1980]. The model can therefore account for secondary phase precipitation/dissolution reactions and calculate glass dissolution rates during reaction progress.

Glass corrosion is rapid initially (see Fig. 1-2) and slows with time as the glass dissolves and dissolved glass species build up in solution. Grambow has termed the early rate as the "forward rate" and the later, slower rate as the "long-term rate" (note: the term "saturation rate" is also used). The forward rate corresponds to the rate when the affinity term, $(1 - Q/K)$, has a magnitude near one, so that there is no slowing of the rate due to buildup of silica and other glass species in solution. The long-term rate corresponds to the rate at longer time periods when the affinity term is much smaller than one. The physical mechanism that determines the magnitude of the long-term rate, is less well defined. This is one of the remaining uncertainties in modeling glass corrosion.

During glass corrosion, the concentration of silica in solution is fixed by a balance between the rate at which silica is released from the glass and the rate at which silica is incorporated into glass alteration layers and secondary phases. Glass corrosion rates increase as the concentration of dissolved silica decreases. Precipitation rates of silica-containing secondary phases increase as dissolved silica increases. Positive feedback between these processes causes the dissolved silica concentration to reach a plateau where dissolved silica is nearly constant with time. Grambow has termed this plateau region the "silica saturation" level for glass. It is clear that the silica saturation level may be a function not only of glass composition but also of other environmental parameters, particularly pH.

The Grambow model has been applied to numerous closed- and open-system dissolution tests of a variety of glass compositions, including both waste glasses and natural glasses [GRAMBOW-1984b, -1984c, -1985, -1987a, -1988a, -1988b, -1990; VAN ISEGHAM-1988; FREUDE-1985; ADVOCAT-1990; STRACHAN-1985; WERME-1990; CURTI-1991; VERNAZ-1992; CROVISIER-1992; MICHAUX-1992; JSS-1987]. In most cases, the model predicts measured trends and agrees with measured solution compositions to within a factor of two (Fig. 3-9). However, the model uses data obtained from actual tests to determine the values of fitting parameters in the model. These parameters include the forward rate constant, final rate constant, silica saturation value, and diffusion constant for silica through the surface layer. The model must therefore be used with caution to simulate a new glass composition different from that for which the model parameters were obtained.

The Grambow model has also been applied to model glass corrosion in saline brines [GRAMBOW-1990, -1991a]. The model has been incorporated into the EQ3/6 code [WOLERY-1979] and uses Pitzer's equations for calculating speciation in brines [JACKSON-1985]. Calculations of solution pH and mineral saturation indices in brines are difficult because of the limitations of current methods for calculating thermodynamic properties of brines, in particular pH. In contrast to dilute solutions, glass dissolution in Mg-rich brines is accompanied by a decrease in pH from initial values of about 7 to values of less than 4. Model results are able to reproduce this trend through the precipitation of Mg-rich alteration phases such as saponite and Mg-zeolites [GRAMBOW-1990].

Fig. 3-9. Predicted vs. Measured Concentrations of Elements Leached from JSS-A Glass at 90°C in Deionized Water vs. Time in Days; Surface Area to Volume Ratio of 10 m^{-1} . Predictions made using the Grambow model (GLASSOL+PHREEQE). NL refers to concentrations normalized to elemental concentrations in the glass. The model predicts most concentrations to within a factor of two. Model results also include the types and masses of precipitated secondary mineral phases (adapted from [GRAMBOW-1987a]).

3.3.2.2.2 Other Models Based on Dissolution Control

A variation of the Grambow model was developed by Bourcier et al. [BOURCIER-1989, -1990b]. The Bourcier model differs mainly in assuming that the rate of reaction is controlled by the affinity for dissolution of the hydrous surface alteration (gel) layer on the reacted glass and does not include provisions for the rate of diffusion through surface layers. The composition of this layer, determined from SIMS or some other surface analytical method, is used to determine thermodynamic properties of the layer. The layer is commonly depleted in alkali elements and B and fairly rich in silica content relative to the unreacted glass. Thus, the model is similar to Grambow's in that predominantly dissolved silica affects the saturation state (and therefore the glass corrosion rate) of the surface layer. However, the model predicts that components other than silica such as Al and Fe of the alteration layer can affect glass corrosion rates. The Bourcier model is incorporated into the EQ3/6 geochemical modeling code [WOLERY-1979]. The results of using this model to predict dissolution rates of SRL 165 glass are shown in Fig. 3-10. The experimentally observed release trends are reproduced by the model, and the solution concentrations calculated are within a factor of two of the measured values.

Fig. 3-10. Predicted vs. Measured Concentrations of Elements Leached from SRL 165 Glass at 150°C in 0.003 M NaHCO₃ Solution with S/V = 0.01 cm⁻¹. Silica concentrations x 0.1. Lines are concentrations predicted by gel layer glass dissolution model (adapted from [BOURCIER-1990b]); symbols are experimental data. Predicted concentrations are generated from starting solution composition, composition of surface gel layer, and rate constant derived from a flow-through glass dissolution experiment.

In the Bourcier model, the thermodynamic properties of the layer are calculated on the basis of a solid solution of amorphous and hydrous phases, whose net composition is that measured for the alteration layer. Phases such as amorphous silica, amorphous ferric hydroxide, and amorphous aluminum hydroxide are used as components in the solid solution model for the alteration layer. The free energy of the alteration layer, as determined from the solid solution model, provides the value of K (see Section 3.3.2.2). The model can be used to make predictions of long-term dissolution rates, but, because compositions of alteration layers must be known to apply the model, some assumptions must be made. These layers can be assumed to be similar to those measured in short-term tests, or data from natural analogues may be used. The model of Bourcier et al. [BOURCIER-1990b] also uses a pH-dependent, short-term rate constant derived in independent flow-through tests. The model can be used to predict glass corrosion rates without any parameters generated from the experiment to be modeled, provided the composition of the alteration layer is known. Use of this model in long-term predictions is limited by the need for assumptions concerning the evolution of the composition of the surface layer with time, the types of secondary phases likely to form, and the lack of any diffusion control of reaction rates.

The DISSOL model [FRITZ-1981] is similar to the Grambow model in that it couples a reaction path geochemical modeling code to a first-order kinetics rate law. The model incorporates a complex clay solid solution model "CISSFIT" [TARDY-1981]. Advocat et al. [ADVOCAT-1990] describe the use of the DISSOL code in simulating R7T7 glass dissolution experiments.

3.3.2.2.3 Modeling Glass Composition Effects

Some attempts have been made to incorporate glass compositional effects into mechanistic glass corrosion models. The hydration theory for determining glass durabilities [PAUL-1977; PLODINEC-1984; JANTZEN-1991] has been used to correlate short-term glass corrosion rates with an estimated free energy of hydration of the glass. The thermodynamic properties of the glass are approximated by a mixture of simple oxides that have a bulk composition the same as the glass. Hydration theory must be combined with a rate law to utilize it in modeling glass corrosion rate. It has been incorporated into mechanistic models in two different ways: to calculate the forward rate constant (k_f) and to calculate the affinity term in the rate expression.

For glass corrosion models that use a rate equation based on transition-state theory, glass composition can affect the rate of glass dissolution in one or more of three ways: (1) the rate constant (k_f) may depend on glass composition; (2) glass composition determines the composition of the surface layers, which in turn is used in the affinity term calculation and therefore affects the dissolution rate; and (3) the glass composition affects the types and amounts of secondary phases that precipitate, which in turn affect the concentrations of species in solution and therefore the size of the affinity term in the rate equation. For corrosion models based on mass transport through the surface layers, the glass composition can influence the corrosion rate by influencing the surface layers and in particular the effective diffusion coefficients for mass transport across these layers.

Grambow [GRAMBOW-1984a] used hydration theory to calculate the glass compositional dependence of k_f with the expression

$$k_f = X \exp(-E_a/RT) \exp(-\Delta G_r(\xi)/RT) \quad (13)$$

where E_a is the activation energy for dissolution (determined experimentally), ΔG_r is the hydration-free energy for the glass dissolution reaction, and ξ is a reaction progress parameter. The first term in the equation, $X \exp(-E_a/RT)$, is an Arrhenius term that accounts for the effect of temperature on the rate constant. The second term, $\exp(-\Delta G_r(\xi)/RT)$, corrects the rate constant for the effect of glass composition. This approach has had limited success when dealing with the compositional range of real waste glasses. It was eventually dropped from the Grambow model and replaced with experimentally determined values for specific glass compositions [GRAMBOW-1987a].

An alternate approach to account for glass composition in the rate expression was used by other workers [BOURCIER-1990a; ADVOCAT-1990]. The effect of glass composition was entered into the affinity term of Eq. 5. In this approach, Q corresponds to the activity product for the dissolution reaction of the entire glass and K is the equilibrium constant for glass dissolution calculated using the free energy of glass hydration. Both Bourcier and Advocat et al. [BOURCIER-1990a; ADVOCAT-1990] added a term to the free energy of hydration to correct for the mixing entropy of the oxide components. They found that this did not improve the ability to simulate experimental measurements. In both studies, the rate of corrosion was not predicted to slow down as

is observed in experiments. Instead, the glass never approaches saturation so that the affinity term has a value of one throughout the simulation. The predicted reaction rate therefore remains approximately constant, in contrast with experimental results. Concentration vs. time curves for elements such as Si and B are predicted to increase linearly with time rather than exhibiting the concave downward shape typical of experimental results. In both cases, the models failed to make accurate predictions of the effect of glass composition on glass dissolution rates.

Another method for applying the hydration-free energy model to glass corrosion is to assume that the rate-limiting step in glass corrosion is the dissolution of the surface alkali-depleted hydrous layer. The thermodynamic properties of this layer can be approximated by assuming it is a solid solution of amorphous components [BOURCIER-1990b]. In this method, the hydration-free energy is computed using the composition of the surface alteration layer rather than the unreacted glass, and the components are chosen to be amorphous rather than crystalline so as to be structurally and energetically more similar to the amorphous surface layer. This model better predicts the experimental glass corrosion rates than does the hydration-free energy model applied to the unaltered glass. However, the relationship between starting glass composition and glass corrosion rate in this model is complex. The composition of the alteration layer (which is used to calculate the glass dissolution affinity and therefore corrosion rate) is affected by both glass composition and solution composition. No attempt has yet been made to quantify this effect in the glass corrosion model. The composition of the alteration layer is determined experimentally from reacted glasses and used as model input.

3.3.2.2.4 Effects of Secondary Phases

The secondary phases that form in glass corrosion tests or the rates at which they nucleate and grow cannot currently be predicted. Reaction path programs can predict the thermodynamically most stable phases, but they rarely predict the phases actually observed in the tests. Current modeling is usually performed with a restricted set of phases known to form in real systems [GRAMBOW-1987a].

One implication of the surface-reaction-controlled model is that precipitation of stable secondary phases at some future time may decrease concentrations of some elements in solution, such as Si. A reduced Si concentration should cause glass dissolution rates to rise [BOURCIER-1990b]. This could explain the rate increases that are illustrated in Fig. 1-2 and discussed in Volume II, Section 2.3.3. Therefore, as early metastable phases follow the Ostwald step rule and convert to more stable phases, glass corrosion rates may rise. Some experimental data have shown such behavior [PATYN-1989; FENG-1993; EBERT-1992]. Some glass compositions rich in Al tend to react to form analcime as a secondary phase. Although the Al-rich glasses are initially more durable, analcime saturation establishes a relatively low dissolved silica concentration compared with Al-poor glasses that are not accompanied by analcime precipitates. Under these conditions, the Al-rich glasses dissolve faster than Al-poor glasses [STRACHAN-1990; VAN ISEGHEM-1988]. As discussed in Volume II, Section 2.1.3.2, the development of more stable secondary phases and the associated increase observed in the corrosion rate for nonradioactive glass were not observed when a similar radioactive glass was tested [FENG-1993].

It may not be necessary to know the exact identities of the precipitating phases. Bourcier compared simulation results using secondary mineral phases observed in tests with simulation results that allowed the thermodynamically most stable phases to form [BOURCIER-1991]. The solution compositions were different in the two simulations, but the overall effect on the rate of glass dissolution was relatively small. The Grambow model predicts that the corrosion rate will be two times faster for the stable-phase assemblage, because of the lower silica concentration, whereas the

model of Bourcier et al. predicts that the rate will be increased by 20% [BOURCIER-1990b]. The effect is smaller in the latter model because the dissolution rate is assumed to be affected by all components of the gel layer, including Fe and Mg which are at higher concentrations in the stable-phase-equilibrated solution. In both cases, the effect is predicted to be not very large, a factor of two greater in one case and 20% greater in the other case.

Another important issue concerning secondary phases is the question of how readily they incorporate radionuclides into their structures. Although some radionuclides are known to partition strongly into the surface layers [PETIT-1990a; BUCKWALTER-1982], more work is needed on the solubilities of radionuclides in host mineral phases to determine whether the radionuclides remain incorporated in the structures after these initially amorphous phases crystallize into distinct phases upon aging.

3.3.2.2.5 Effects of Other Materials

Many experimental studies have looked at the effects of other repository materials on glass corrosion rates; i.e., with tuff present [BIBLER-1985; ABRAJANO-1988b; BAZAN-1987; BATES-1987, -1988, -1989a, -1989b], with Fe or stainless steel present [McVAY-1983; MENDEL-1984; HERMANSSON-1985; BURNS-1986; BART-1987], with bentonite present [HERMANSSON-1985; WANNER-1986] and with Pb and other metals present [BUCKWALTER-1982; LEHMAN-1985; BURNS-1986]. Reviews of repository material-glass interactions are found in Bibler et al. [BIBLER-1987] and Werme et al. [WERME-1990]. The results of these studies are discussed in Volume II, Section 4.

Modeling the effects of repository materials on glass corrosion has received much less attention. The Grambow model has been used to simulate the effect of Fe corrosion products on glass corrosion [GRAMBOW-1987b]. The results indicate that the increase in corrosion rate of glass caused by adding Fe to the system was probably due to the precipitation of iron silicate phases or colloids that effectively removed silica from solution. Alternatively, sorption of silica onto the iron oxides could have taken place. The relatively high corrosion rates were therefore caused by the lowering of silicic acid in solution and consequent increase in the affinity term $[1 - ([H_4SiO_4]_s/K)]$ in Eq. 10.

The effect of bentonite on glass corrosion was modeled by Grambow et al. [GRAMBOW-1986b, -1986d]. The results suggested that the early increase in leach rate observed in experiments was due to a delayed approach to silica saturation that takes place with bentonite present. Long-term effects should be less significant. The rate of glass corrosion also is closely linked with the amount of bentonite surface area available for ion exchange.

3.3.2.2.6 Effects of Radiolysis

Radiolysis of the local environment surrounding the glass waste form appears to have a complex effect on glass corrosion (see Volume II, Section 2.5). The major effect is the formation of nitric acid from gaseous nitrogen in a humid atmosphere [VAN KONYNENBURG-1986]. Models for glass corrosion can account for the effect of nitric acid on the pH and Eh of the local environment by adding nitric acid and hydrogen peroxide into the system at a rate determined from theoretical or experimental data on nitric acid and oxidant production rates. The effect is likely to be small because of the pH buffering capacity of other components in the system, in particular, the host rock and glass waste form.

Possible radiation-induced structural damage to the glass does not appear to alter the corrosion rate of the glass (see Volume II, Section 2.5). Any radiation damage induced in the glass by a gamma radiation field is therefore not expected to affect the overall glass corrosion rate or mechanisms as predicted by current models. Because glass is already a disordered phase, radiation-induced defects and dislocations are not expected to be important for glass durability.

3.3.3 Natural Analogues and Model Validation

Interpretations of the chemical evolution of glasses in natural environments are inherently difficult because of the lack of key environmental data (see Volume II, Section 5.0) such as the time period a particular glass was exposed to water, the composition of the water, and the values of physical parameters such as temperature and relative humidity. Although in many cases, reasonable values can be assumed, these assumed values will necessarily restrict application for quantitative validation of corrosion models. In addition, the output of corrosion models that best constrains the goodness of fit of the model is solution compositional data, which obviously are not available for natural analogue sites. As a consequence, most applications of chemical models to natural glasses are restricted to validation of reaction path models (or observations based on short-term experiments) for predicting the identities of secondary phases found associated with the glass. The exceptions are modeling simulations of the corrosion of natural glasses (such as basalts) in laboratory leach experiments [CROVISIER-1987; JANTZEN-1986b; MAZER-1987].

Attempts to model glasses in natural environments include use of the GLASSOL code [GRAMBOW-1986c; McGRAIL-1988], EQ3/6 [BERGER-1987], and DISSOL [FRITZ-1981 in CROVISIER-1992]. In most cases, agreement to within a factor of two is found between observed and predicted secondary phase assemblages once allowances are made for suppressing some thermodynamically stable phases to allow metastable precipitates to form. The modeling of Crovisier et al. also provided for estimates of mass balances for altered basalt glasses in Iceland and found good agreement between model-predicted results and field observations [CROVISIER-1992].

3.3.4 Linkage between Models of Glass Corrosion Rate and Repository Performance Assessment Models

Current performance assessment strategies are usually probabilistically based and do not explicitly account for chemical and physical processes that will govern repository behavior [LIEBETRAU-1987; SHAW-1990; McGRAIL-1993]. Efforts to perform deterministic performance assessments are far from being mature [O'CONNELL-1986; MOUCHE-1988, -1990]. Most calculations to date have assumed glass corrosion rates that are either constant [UMEKI-1986; STRACHAN-1990], a function of temperature [CHAMBRE-1988], solubility-controlled [NAS-1983; STRACHAN-1990], or controlled by external field mass transfer [PIGFORD-1985]. An example of a performance assessment calculation that includes a kinetic glass dissolution model is provided by McGrail [McGRAIL-1993]. This performance assessment model couples a Grambow-type glass dissolution model with a transport model and also incorporates the influence of other materials in the engineered barrier system. The results show that models which assume solubility constraints on radionuclide concentrations may not be conservative. Experimental data for waste glass dissolution show that measured actinide concentrations can be orders of magnitude higher than the dissolved actinide concentrations [BATES-1992a], due to formation of colloids containing actinides.

Curti has used the Grambow model to simulate dissolution of the British MW glass in order to critically evaluate the model for use in performance assessment of the Swiss high-level waste repository [CURTI-1991]. Curti concluded that the model is not yet suitable for safety analysis for the following reasons: "(1) the model neglects the potential effects of diffusive transport and silica sorption in a bentonite backfill on the glass corrosion kinetics; (2) the release of radionuclides can only be modeled assuming congruent dissolution; and (3) the magnitude of the final rate of corrosion, the parameter defining the maximal lifetime of the glass matrix, is still not known with sufficient precision." [CURTI-1991].

Curti's first point has to do with the observation that the British MW glass reacts to form a thick silica-rich layer on the surface, unlike the glasses for which the model was developed and applied. The presence of a bentonite backfill was found to promote precipitation of an amorphous silicon-rich layer on the glass surface. Without accounting for this precipitated silica layer, the model will predict "silica saturation" much earlier than actually occurs in experiments and incorrectly predicts a much slower dissolution rate than observed in experiments. Curti added a fictitious silica phase to the PHREEQE database to account for this silica layer [CURTI-1991]. The basic problem in this approach is that the Grambow model does not yet include a sorption isotherm for silica in the surface layer.

The second point is that the model makes the conservative assumption that the integrated release rate of radionuclides will be limited by the cumulative amount of glass corrosion. Although the assumption is valid, the model ignores the fact that some radionuclide leachate concentrations will likely be limited by low solubilities and will not be released at the relatively high rate of glass network corrosion [MARPLES-1991]. It is conceivable that the geochemical model PHREEQE could account for the lowered release rates of radionuclides, provided adequate thermodynamic data were available for the solids into which they are incorporated. Current programs are in place in several countries to obtain the necessary data. This criticism is valid for all glass corrosion models and is not specific to the Grambow model.

The third point is the most significant. The Grambow model (as is true for all current glass corrosion models) does not provide a mechanistic basis for predicting the long-term corrosion rate of glass. In the Grambow model, the final rate of corrosion is a fitting parameter obtained from short-term, high-S/V test results (the high S/V presumably accelerates tests to equivalent long times; see Volume II, Sections 2.3 and 3). The concept of "residual chemical affinity," an ad hoc term used by Grambow to justify adding the long-term rate parameter (R_{∞} in Eq. 12) to his rate equation, has also been criticized by Petit et al. [PETIT-1990b]. In Petit's experiments, both powdered and monolithic glass samples were reacted in a common vessel and showed a continuous slowdown in corrosion rate past the point where silica saturation occurred and where the rate should have remained constant. Petit et al. [PETIT-1990b] concluded that the mechanism controlling the long-term rate is affected by other environmental parameters and that alkali concentrations as well as silica concentration must be included to explain the experimental results. Grambow [GRAMBOW-1992] has since suggested that the long-term corrosion, after the solution becomes saturated, may be controlled by water diffusion into the glass or by nucleation and precipitation of secondary phases.

Chemical processes involving multiple repository materials are not mechanistically linked in any of the current performance assessment modeling approaches. There is no feedback to glass corrosion submodels. For example, the effects of the corrosion of stainless steel canisters on solution pH and Fe concentrations, which are known to influence glass corrosion rates, have not been incorporated into performance assessment modeling. Likewise, the response of glass to environmental changes induced by metal corrosion processes will affect subsequent corrosion rates and mechanisms for other repository materials. Because of such interactions, implementation of mechanistic glass corrosion models for predicting long-term corrosion and weathering rates in performance assessment is a significant challenge.

4.0 SUMMARY OF UNCERTAINTIES

An overview of the remaining uncertainties in understanding (1) corrosion and weathering rates and (2) radionuclide release rates is presented in Sections 4.1 and 4.2. The significance of these uncertainties is addressed in Section 4.3.

4.1 Uncertainties in Waste Glass Corrosion and Weathering

The remaining uncertainties can be addressed by considering the uncertainties associated with the three stages of glass corrosion identified in Section 1.2.2. For Stages 1 and 2 the uncertainties arise from uncertainties in experimental measurements and uncertainties associated with the extrapolation and interpolation of experimental data to span the full range of glass compositions and environmental conditions of interest. Another important uncertainty associated with the communication of glass corrosion and radionuclide release information is the lack of standardization of definitions of terms such as "release" and of some laboratory testing methods. For Stage 3 the uncertainties are modeling uncertainties associated with extrapolation into the distant future.

As discussed in the preceding sections of this volume and throughout Volume II, a wide body of experimental data shows that corrosion and weathering rates depend on glass composition and environmental factors. The available data extensively populate most of the factor space defined by the range of anticipated glass compositions and environmental conditions discussed in Section 2.2. The experimental uncertainties are generally less than 50% and are probably smaller than the uncertainties associated with the use of models to interpolate and extrapolate experimental data to cover conditions (e.g., weathering) where the data are fairly sparse. For example, there are not a lot of data for the weathering rate of waste glass under the low relative humidity conditions that would occur at temperatures above 100°C in an unsaturated repository.

Evidence for the adequacy of the current understanding of waste glass corrosion during stages 1 and 2 is provided by the extent to which the qualitative and quantitative effects of compositional and environmental factors can be interpreted and modeled in terms of the underlying physical and chemical processes. The evidence suggests that the corrosion and weathering reactions involve ion exchange of network modifiers, hydrolysis of the glass network, dissolution of glass components, nucleation and precipitation of secondary phases, and associated mass transport (diffusion) of reactants and products through the glass network and surface layers. Mass transport through the surface layers may be influenced by restructuring, dissolution, cracking, spallation, and exfoliation. Some of these reaction processes are coupled, which complicates the interpretation of experimental results. Under most experimental conditions, however, it appears that the overall rates of corrosion and weathering are controlled by the rate of dissolution reactions at the glass surface, although there is evidence for control by mass transport through the surface layers under some circumstances. The application of transition-state theory to modeling the rate-limiting surface reactions has been successful in interpreting experimental observations (see Section 3). Although this success indicates that our current understanding is, in general, qualitatively correct, there are several uncertainties associated with implementing these models for applications such as predicting the corrosion rates in a repository and determining the dependence of the corrosion rate on glass composition.

Current models include parameters that must be empirically determined by regression from experimental data. Although the models may be theoretically sound, quantitative uncertainties may be introduced by these parameters. For example, the forward reaction rate constant in dissolution models has not been determined as a function of temperature and solution composition. In addition, uncertainties concerning the dissolving phase and in reaction path model predictions of the secondary mineral phases that control the leachate composition affect the determination of the dissolution affinity. Also, utilization of mass transport models is complicated by uncertainties concerning when the surface layers become protective and by the effects of the surface layer properties (thickness and effective diffusion coefficients) and behavior (cracking and exfoliation) under aqueous corrosion and weathering conditions.

When kinetic parameters measured currently in the laboratory are extrapolated to estimate the corrosion of minerals in natural systems, they predict rates of reactions up to several orders of magnitude faster than those observed in nature [VELBEL-1986]. Several reasons for the slower rates in natural systems have been proposed: (1) the minerals do not remain in contact with water or are isolated from water flow, thereby affecting estimates of true reaction times; (2) the mineral surfaces are poisoned by adsorbed species (for example, phosphate adsorbed on calcite surfaces drastically reduces the dissolution rate); and (3) surface layers form on the mineral surfaces and armor the minerals from further reaction. The reasons for this discrepancy should be established in order to know whether a similar decrease in the corrosion rate is to be expected when utilizing glass corrosion rates measured in the laboratory for assessing the corrosion rates in a repository. Field testing studies (see Volume II, Section 4.1) are relevant to investigating the possible discrepancies between natural systems and laboratory tests. Studies of natural analogues for glass (such as basaltic glass [EWING-1987]) may also help in this regard (see Volume II, Section 5.0).

Mechanistic models for predicting the corrosion rate of waste glass have not yet matured to the point that they are useful for predicting glass durability as a function of glass composition. Although the theoretical foundation for the models [AAGAARD-1982; RIMSTIDT-1980] is well established, uncertainties in our understanding of the dominant rate-controlling mechanisms as a function of glass composition and environmental conditions make it impossible, for now, to rigorously incorporate glass compositional terms into equations describing glass corrosion. It may also be necessary to include the effects of glass water content, glass structure (such as the existence of percolation pathways), secondary phases, and perhaps other effects of glass composition on glass reaction rates. In particular, the effects of waste glass composition on the secondary phases that form at high reaction progress and how these phases, in turn, influence the corrosion rate need to be clarified through appropriate experiments and modeling.

For Stage 3 some additional uncertainties are involved. The ASTM standard practice entitled "Prediction of the Long-Term Behavior of Waste Package Materials Including Waste Forms Used in Geologic Disposal of High-Level Nuclear Waste" [ASTM-1991] provides a useful framework for discussing these uncertainties. This practice identifies an iterative testing and modeling process for predicting the long-term behavior of materials. In simplified terms, it involves (1) identifying alteration processes, (2) conducting a variety of tests to support model development (including experimental measurement of model parameters), and (3) performing model validation.

Consistent with this general framework, the Stage 3 modeling uncertainties include those involved in identifying the physical and chemical processes that control the long-term rate and in model validation. The ultimate chemical process responsible for controlling the long-term dissolution rate has not been identified. The Grambow model includes the concept of "residual affinity," which is

used to explain the continued dissolution even after "silica saturation." This approach has no mechanistic basis and therefore cannot be quantified in the model, except as a fitting parameter to short-term test results. The model of Bourcier et al. [BOURCIER-1990b] predicts the long-term rate on the basis of the solution saturation with respect to the surface alteration layer. This model avoids the concept of residual affinity, with the implicit assumption that the affinity effect caused by the depletion of elements from solution as a result of from secondary phase formation will always be much greater than any effect from the glass inherently being a thermodynamically unstable solid. In other words, the solution will never become saturated with respect to the gel layer, so there is no need to try to determine how fast glass will dissolve under conditions approaching saturation.

Recently, Grambow [GRAMBOW-1991b] has suggested that two long-term rate-controlling processes occur under silica saturation conditions. The first involves the long-term nucleation and precipitation of secondary phases, which act as sinks for silica and thereby control the residual affinity for the rate-limiting matrix dissolution reactions. The second assumes that, as the affinity for the dissolution reactions decreases, the rate of these reactions will decrease to the point at which other processes, such as the water diffusion-controlled ion-exchange process, become dominant. A general model should, therefore, incorporate provisions to allow these processes to become dominant at the appropriate time in long-term simulations.

Both nucleation and growth kinetics for secondary phases need to be added to the simulations. Current modeling work assumes that secondary phases precipitate immediately upon reaching saturation in solution. It is commonly observed that phases do not begin to precipitate until they are sufficiently supersaturated that they can overcome any nucleation barrier to precipitation. Precipitation rates are sometimes slower than the buildup in species concentration and precipitation kinetics must be added to the simulations to account for this. Uncertainties remain with regard to both the secondary phases that precipitate in the long term as well as the nucleation and precipitation kinetics, and these areas need further investigation. In particular, the effects of glass composition and interactions with other materials that may result in precipitation of secondary phases which can increase the dissolution affinity need further investigation.

4.2 Uncertainties in Radionuclide Release Rates

Thermodynamic and kinetic approaches can be used to determine the release rates of radionuclides from waste glass. The thermodynamic solubility-controlled approach can be used to calculate the release rates of the sparingly-soluble radioelements. It assumes that the concentration of the sparingly-soluble radioelements is limited by the solubility of a specific solid phase. The solubilities may be calculated from thermodynamic data or determined from solubility measurements. Although the thermodynamic or "solubility-controlled" approach is not addressed in detail in this document, the available data on formation of colloids in waste glass aqueous corrosion and weathering (see Volume II, Sections 2.7.3 and 3.6) suggest that both solutes and colloids should be considered when the concentrations of sparingly-soluble radioelements in the immediate vicinity of the waste glass are considered. However, a complete treatment of the solubility-controlled approach and the associated uncertainties are beyond the scope of this document.

The kinetic approach involves estimating the rate of release of individual radioelements based on the rate of glass corrosion and radionuclide retention in the surface alteration layer. The uncertainties in the cumulative release are determined by the uncertainties in the glass corrosion and weathering rates, as discussed in Section 4.1 above. In reality, the radionuclide release rates will be lower because of the incorporation of radionuclides into secondary phases. Empirical observations on

the retention of radionuclides in surface alteration layers during waste glass corrosion and weathering are discussed in Volume II, Sections 2.7.2 and 3.6. Models to simulate incorporation of actinides into surface layers are not available. The extent to which it is appropriate to utilize the empirically determined retention factors for extrapolations into Stage 3 is uncertain. A better understanding of the chemical (e.g., adsorption and coprecipitation) and physical (e.g., surface layer spallation and colloid formation) effects involved are needed for confident extrapolation.

Validation of our current understanding and models continues to be a major source of remaining uncertainty concerning radionuclide release associated with the long-term weathering and corrosion of waste glass. Because, as acknowledged by the NRC [NRC-1986], long-term predictive models cannot be "validated" in the ordinary sense of the word, some of the uncertainty associated with model validation is associated with determining what constitutes a sufficient validation.

4.3 Significance of Remaining Uncertainties

As indicated by the above discussion, there are many uncertainties associated with obtaining accurate predictions of waste glass corrosion and associated radionuclide release rates. However, to put the importance of these uncertainties into the proper perspective, the need for more accurate and precise information should be considered.

There are no established regulatory or other standards that the corrosion rate and associated radionuclide release rates of waste glass in a repository have to satisfy. In lieu of such standards, it is instructive to consider how the corrosion of waste glass logs and the associated fractional radionuclide release rate per year, based on short-term experimental data, compare with the allowed annual fractional release rates from the EBS [NRC-1986] (see Section 1.2.4). While the estimates presented in Section 1.2.4 are not intended to address questions concerning the adequacy of borosilicate glass as a waste form, they are instructive insofar as they indicate that waste glass may be a very effective barrier if the values used for the corrosion rate and retardation factors can be justified and extrapolated into Stage 3 of the waste glass corrosion process. As pointed out in Volume II, Sections 2 and 3, there are many glass compositions and environmental factors (e.g., radiolysis and interaction with other materials) that may cause waste glass corrosion rates to be higher or lower than the value of 2.5×10^{-3} g/m²/d used in Section 1.2.4 (see, for example, Volume II, Section 2.3.4).

For extrapolation of the experimental results into Stage 3 the current theoretical understanding and empirical evidence indicate that glass corrosion rates should generally decrease with time. This is because the buildup of corrosion products in solution and on the surface of the glass will, in general, inhibit the corrosion process. However, effects such as onset of nucleation and precipitation of secondary phases, increased water flow rate, and cracking of protective layers may give rise to increases in the rate. While such effects introduce uncertainties in accurate long-term corrosion predictions, they are sufficiently well understood that predictions, based on the assumption that the measured "saturation rates" can be used to provide an upper bound on the long-term rates, can be made with some confidence [GRAMBOW-1991b] if care is taken in developing the glass composition and in repository design to avoid effects that can lead to excursions in the glass corrosion rate. The use of less conservative assumptions to obtain more realistic (and probably lower) estimates of the corrosion rate would increase predictive uncertainty (i.e., the use of lower point value estimates would increase the probability that the actual value would exceed the point value estimate used). Pigford [PIGFORD-1985] has pointed out that "desire for greater realism must be balanced against increasing uncertainties in prediction and loss of reliability."

Reduction in the experimental and modeling uncertainties are important to support the use of the measured "saturation values" of the corrosion rates and empirical radionuclide retention factors for long-term predictions. More specifically, uncertainties associated with the high temperature ($>100^{\circ}\text{C}$) weathering as a function of relative humidity and the effects of fragmentation or spallation of the surface layers on radionuclide retention under weathering need to be addressed.

Despite the remaining uncertainties, the available laboratory data, data from natural analogue glasses, and the theoretical understanding of corrosion processes summarized in Volumes I and II of this document provide no evidence to suggest that HLW borosilicate glass is not suitable for disposal in suitably engineered systems or to reconsider the judgments made in various countries throughout the world that borosilicate glass is a suitable waste form material for high-level nuclear waste. In fact, the available data indicate that properly formulated borosilicate glass waste is a corrosion-resistant material that should be effective in inhibiting the release of radionuclides under a wide variety of conditions. However, this does not mean that the suitability of waste glass for geologic disposal has been, or can be, established from the data presented here alone; this would require performance assessment. It would also require comparison of the assessed performance with a variety of performance standards that may be used in making a judgment concerning the level of waste glass performance needed to establish suitability for disposal. However, as pointed out in the Preface, the scope of this document is not intended to include comparisons of waste glass chemical durability with any objective or subjective standards that interested parties may use in making a judgment that borosilicate glass waste forms are "acceptable for disposal."

Although borosilicate waste glass is a robust waste form, the designers of waste packages for geologic disposal of high-level waste glass should consider the uncertainties associated with the effects of high temperature ($>100^{\circ}\text{C}$) weathering conditions on waste glass corrosion and radionuclide release. Also, the effects of engineered barrier materials and glass constituents (e.g., iron and aluminum) on the dissolution affinity, and hence long-term corrosion of waste glass, should be considered in the choice of waste package materials and in establishing waste glass composition envelopes.

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APPENDIX A**COMPOSITION FOR REFERENCE NUCLEAR WASTE GLASSES**

The appendix compiles the compositions for reference borosilicate glasses mentioned throughout the text of Volumes I and II.

Table A-1. Composition (wt %) for Reference Nuclear Waste Glasses

Oxide	SRL 131 ¹	SRL 165 ¹	SRL 202 ²	SRL 165 SA	PNL 76-68 ¹	WV 205 ¹
SiO ₂	44.33	52.0	49.0	55.7	40.84	45.20
Al ₂ O ₃	10.77	6.05	3.8	11.7	0.60	3.31
B ₂ O ₃	11.37	8.98	8.0	8.4	8.81	9.96
Li ₂ O	3.16	4.33	4.2	---	---	3.05
FeO	2.42	2.76	---	---	1.95	---
ZnO	---	---	---	---	---	---
MnO	2.45	2.27	2.0 ³	---	0.05	---
Na ₂ O	---	---	8.9	18.2	11.70	11.03
K ₂ O	---	---	3.7	---	0.13	3.51
CaO	1.53	1.82	1.2	6.0	2.36	0.61
MgO	1.43	0.97	1.3	---	0.15	1.31
UO ₂	2.13	1.19	1.9 ⁴	---	---	---
Fe ₂ O ₃	8.95	10.22	11.4	---	7.23	11.84
ZrO ₂	0.48	0.72	0.1	---	1.68	3.12
P ₂ O ₅	0.01	0.00	---	---	0.74	2.25
TiO ₂	0.73	---	0.9	---	3.03	0.97
Cs ₂ O	---	---	---	---	1.02	0.10
NiO	0.96	1.26	0.82	---	0.25	0.70
Nd ₂ O ₃	---	---	---	---	6.82	---
SrO	0.05	0.06	---	---	0.42	0.12
Cr ₂ O ₃	0.18	0.20	---	---	0.15	0.22
BaO	---	---	---	---	0.53	0.06
Other						

¹From [GELDART-1988].²From [JANTZEN-1992].³As MnO₂.⁴As U₃O₈.

Table A-1 (Contd.)

Oxide	YN500 ⁵	YN600 ⁹	R7T7 ⁶	UK209 ¹	SON64 ⁷	SM58 ⁷
SiO ₂	42.19	45.00	45.48	50.88	47.16	56.87
Al ₂ O ₃	3.43	3.60	4.91	5.11	1.69	1.16
B ₂ O ₃	13.72	14.20	14.02	11.12	18.42	12.28
Li ₂ O	2.95	3.00	1.98	3.99	---	3.74
ZnO	1.97	3.00	2.50	---	---	---
MnO ₂	0.51	0.37	0.72	---	---	---
Na ₂ O	8.39	10.00	9.86	8.30	12.53	8.30
K ₂ O	1.97	---	---	---	---	---
CaO	1.97	3.00	4.04	---	---	3.83
MgO	---	---	---	6.34	---	2.05
U ₃ O ₃	---	---	0.52 ⁸	0.06	0.45	---
Fe ₂ O ₃	7.41	2.04	2.91	2.73	5.07	1.17
ZrO ₂	2.00	1.46	2.65	---	---	---
P ₂ O ₅	0.40	0.30	0.28	---	---	---
TiO ₂	---	---	---	---	---	4.45
CeO ₂	2.02	3.34	0.93 ⁹	---	---	---
NiO	0.49	0.23	0.74	0.36	0.24	0.11
Nd ₂ O ₃	1.87	1.38	1.59	---	---	---
MoO ₃	1.98	1.45	1.70	---	---	---
Cr ₂ O ₃	0.49	0.10	---	0.56	0.43	---
BaO	---	3.00	---	---	---	---
Other				9.75 ¹⁰	13.14	6.06

⁵From [YANGISAWA-1987].⁶Also known by the designation SON68; from [NOGUES-1985].⁷From [NOGUES-1985].⁸As UO₂.⁹As Ce₂O₃.¹⁰Fission Product Oxides.

Table A-1 (Contd.)

Oxide	WGI124 ¹¹	C31-3 ¹²	SM527	GP-12 ¹³
SiO ₂	70	34.75	38.75	46.2
Al ₂ O ₃	2	10.28	19.96	2.5
B ₂ O ₃	---	4.14	21.70	13.4
Li ₂ O	---	0.98	3.10	3.4
ZnO	---	4.90	---	---
MnO ₂	---	---	0.02	---
Na ₂ O	4	3.12	8.64	4.0
K ₂ O	1	---	---	---
CaO	5	3.84	3.87	2.5
MgO	5	1.44	0.14	1.5
U ₃ O ₃	---	---	0.02	---
Fe ₂ O ₃	6 ¹⁴	.033	0.70	---
ZrO ₂	---	3.08	0.05	1.5
RuO ₂	---	1.28	0.02	---
TiO ₂	1	2.80	1.55	5.0
CeO ₂	---	1.38	---	---
NiO	1	---	---	---
Nd ₂ O ₃	---	2.18	0.07	---
MoO ₃	1	2.36	0.05	---
Cr ₂ O ₃	1	---	0.02	---
BaO	2	15.28	---	---
Other	1	6.43	1.35	20.00

¹¹From [VAN ISEGHEM-1984].¹²From [GRAMBOW-1984].¹³From [SHANGGENG-1987].¹⁴As Fe₂O₂.

Table A-1 (Contd.)

Oxide	DWPF blend ¹⁵	West Valley ¹⁶	NCAW ¹⁷	CC ¹⁷	PFP ¹⁷	NCRW ¹⁷
SiO ₂	50.2	41.0	53.5	63.4	52.5	54.1
Al ₂ O ₃	4.0	6.0	2.2	1.8	3.8	6.5
B ₂ O ₃	8.0	12.9	10.5	10.5	10.5	10.5
Li ₂ O	4.4	3.7	3.8	3.8	3.8	3.8
MnO	2.0	1.0 ¹⁸	0.2	0.9	1.3	---
Na ₂ O	8.7	8.0	11.2 ¹⁹	10.7 ¹⁹	11.0 ¹⁹	10.2 ¹⁹
K ₂ O	3.9	5.0	---	---	---	---
CaO	1.0	0.5	0.8	1.0	3.0	0.8
MgO	1.4	0.9	0.8	1.6	2.8	0.8
U ₃ O ₈	2.1	0.6 ²⁰	1.2 ²⁰	---	---	---
Fe ₂ O ₃	10.4	12.1	7.0	4.3	9.2	0.1
ZrO ₂	---	1.3	3.8	---	---	10.5
TiO ₂	0.9	---	---	---	---	---
ThO ₂	---	3.6	---	---	---	---
NiO	0.9	---	---	---	---	---
Cr ₂ O ₃	0.1	---	---	---	---	---
Other	2.0	3.4	5.0	2.0	2.1	2.7

¹⁵From [SRWCP-1992].¹⁶From [WVWCP-1991].¹⁷From [KRUGER-1990].¹⁸As MnO₂.¹⁹Total reflects (Na₂O + K₂O).²⁰As UO₂.

Table A-1 (Contd.)

Oxide	M7 ²¹	SON ²¹	AVH ²¹	98/12 ²¹	209 ²¹	BNFL ²¹
SiO ₂	46.1	53.9	45.1	48.2	50.0	49.8
Al ₂ O ₃	5.0	1.8	4.9	2.2	5.1	1.6
B ₂ O ₃	14.2	12.3	13.9	10.5	11.1	8.8
Li ₂ O	---	10.0	2.0	---	---	16.7
MnO ₂	---	0.7	---	0.2	---	---
Na ₂ O	14.3	10.8	9.8	14.9	8.3	7.1
CaO	4.1	5.4	4.0	3.5	---	---
MgO	---	---	---	1.8	6.3	13.7
Fe ₂ O ₃	6.5	0.4	2.9	0.2	2.7	0.3
ZrO ₂	0.6	0.5	1.0	1.4	1.4	0.4
ZnO	---	1.5	---	---	---	---
SrO	0.1	---	---	0.3	0.3	---
Cs ₂ O	0.4	---	---	0.7	0.8	---
Other	---	1.2	16.4	---	---	---

²¹From [RAMSEY-1989].

Table A-1 (Contd.)

Oxide	Tokai ²²	JAERI ²²	ABS41 ²²	LRR/ECM ²²	FA2 ²²	204 ²²	AVB/SAN ²²
SiO ₂	43.2	46.2	52.0	50.9	47.3	52.6	45.1
Al ₂ O ₃	3.5	1.8	2.5	2.1	---	---	6.2
B ₂ O ₃	14.1	11.8	15.9	11.2	12.4	7.6	13.3
Li ₂ O	---	---	---	---	---	---	21.2
MnO ₂	0.3	---	0.8	0.2	7.4	---	---
Na ₂ O	8.4	23.4	9.4	12.7	20.0	11.7	10.2
K ₂ O	---	0.7	---	---	---	---	---
CaO	2.0	9.0	---	---	---	---	4.1
MgO	---	4.7	---	---	---	---	---
Fe ₂ O ₃	7.4	0.4	3.6	12.5	3.6	9.6	---
ZrO ₂	2.0	0.5	1.3	0.6	0.6	1.7	---
P ₂ O ₅	---	0.4	---	---	---	---	---
MoO ₃	---	0.4	---	---	---	---	---
SrO	0.4	---	0.3	0.1	0.1	0.4	---
Cs ₂ O	1	---	0.9	0.2	0.4	1.0	---
Other	---	0.6	---	---	---	---	---

²²From [WICKS-1985].

Table A-1 (Contd.)

Oxide	EA Glass ²³	SF12 ²⁴	WVCM44 ²⁵	WVCM50 ²⁵
SiO ₂	48.95	43.4	21.0	20.0
Al ₂ O ₃	3.67	6.1	3.5	5.2
B ₂ O ₃	11.12	11.1	2.9	3.7
Li ₂ O	4.28	3.1	1.3	1.0
MnO ₂	1.34 ²⁶	---	0.8	0.8
Na ₂ O	16.71	12.0	7.4	7.3
K ₂ O	0.04	3.7	2.7	1.3
CaO	1.13	---	0.6	0.6
MgO	1.66	---	0.8	0.5
Cr ₂ O ₃	---	---	0.2	---
Fe ₂ O ₃	8.08	11.3	8.1	8.4
FeO	0.89	---	---	---
ZrO ₂	0.41	2.3	0.3	0.3
ThO ₂	---	---	2.9	3.1
UO ₂	---	---	0.5	0.5
CeO ₂	---	---	---	0.6
TiO ₂	0.71	---	---	---
BaO	---	---	0.2	0.3
NiO	0.61	---	---	---
La ₂ O ₃	0.41	---	---	---
P ₂ O ₅	---	2.3	1.0	1.1
Nd ₂ O ₃	---	---	---	0.1
Other	---	4.7	0.8	0.7

²³From [SRWCP-1992].²⁴From [BUECHELE-1991].²⁵From [EBERT-1991]. All values are in elemental weight percent.²⁶As MnO.

Table A-1 (Contd.)

Oxide	HW-39 ²⁷	ABS-118 ²⁸	MW ²⁸	SAN60 ²⁹	ABS-39 ³⁰
SiO ₂	51.3	45.48	47.1	43.4	48.5
Al ₂ O ₃	4.3	4.91	5.33	18.1	3.1
B ₂ O ₃	9.6	14.02	16.3	17.0	19.1
Li ₂ O	3.8	1.98	3.70	5.0	12.9
MnO ₂	---	0.97	---	---	---
Na ₂ O	10.4	9.86	8.35	10.7	---
CaO	2.9	4.04	---	3.5	---
MgO	0.8	0.04	5.22	---	---
Cr ₂ O ₃	1.3	0.51	0.41	---	---
Fe ₂ O ₃	11.1	2.91	2.61	0.3	5.7
Pr ₆ O ₁₁	0.1	0.49	0.47	---	---
ZrO ₂	0.6	2.61	1.66	---	---
UO ₂	---	0.85	---	---	1.66
SrO	0.1	0.33	0.35	---	---
CuO	0.1	---	---	---	---
CeO ₂	---	0.99	0.98	---	---
ZnO	---	2.50	---	---	---
BaO	0.2	0.58	0.56	---	---
NiO	0.6	0.86	0.27	---	---
SO ₄	0.5	---	---	---	---
F	0.3	---	---	---	---
La ₂ O ₃	0.5	---	---	---	---
MoO ₃	0.3	2.05 ³¹	1.76 ³¹	---	---
Cs ₂ O	0.2	1.10	0.99	---	---
P ₂ O ₅	---	0.28	0.08	---	---
Nd ₂ O ₃	0.5	1.52	1.54	---	---
Other	0.6	1.12	1.03	2.0	9.0

²⁷From [BATES-1989].²⁸From [CURTI-1991].²⁹From [VAN ISEGHEM-1988].³⁰From [WERME-1986].³¹Reported as MoO₂.

Table A-2. International MIIT Waste Form Compositions^a (mole %)

Oxide	U.K. BNFL WG	Germany EMT Pamela	Canada AECL AS	Canada AECL GC	Belgium TRUW 124	Belgium AVS/ SAN 60	France SON 68-18	Japan JAERI Z-20
SiO ₂	54	54	59	53	71	47	53	44
B ₂ O ₃	11	12				16	14	13
ZrO ₂	1	<0.5	<0.5	<0.5		<0.5	1	1
Al ₂ O ₃	3	2	14	5	2	11	3	3
P ₂ O ₅		<0.5					<0.5	1
Na ₂ O	8	9	9	7	4	11	11	23
Li ₂ O	9	9				11	5	
K ₂ O					1			1
MgO	10	3				5		3
CaO		5	15	17	5	4	5	8
CeO ₂	<0.5	<0.5	1	1		<0.5		<0.5
Cr ₂ O ₃	<0.5	<0.5	<0.5	<0.5	1		<0.5	<0.5
ZnO		<0.5					2	
CuO					1			
TiO ₂		4		15	1			<0.5
NiO	<0.5	<0.5	<0.5	<0.5	1		1	<0.5
Fe ₂ O ₃	1		<0.5	<0.5	5		1	1
MnO ₂		1					1	<0.5
MoO ₃	1	<0.5	<0.5	<0.5	1	<0.5	1	1

^aSource: Adapted from [RAMSEY-1989].

Table A-2 (Contd.)

Oxide	SRL 165/28	SRL 131/35	PNL 76-68	RHO HW 39	MCC ARM-1	Basalt	Aged 165/28	Cath. Univ.
SiO ₂	58	47	53	56	52	61	58	52
B ₂ O ₃	5	10	10	9	11		6	10
ZrO ₂	1		1	<0.5	1		1	2
Al ₂ O ₃	3	2		3	4	12	3	2
P ₂ O ₅								1
Na ₂ O	11	14	14	12	10	5	11	12
Li ₂ O	10	8		9	11		10	7
K ₂ O		<0.5						3
MgO	1	2	<0.5	2		7	1	2
CaO	2	2	3	3	3	8	2	1
Na ₂ CO ₃		1						
La ₂ O ₃		<0.5	1	<0.5			<0.5	
CeO ₂				<0.5	1			<0.5
Nd ₂ O ₃			<0.5	<0.5	1			
ZnO			5		1			
TiO ₂		1	3	<0.5	3			1
NiO	1	2	<0.5					1
Fe ₂ O ₃	5	7	5	5	1	7	5	5
MnO ₂	2	4	<0.5	<0.5		<0.5	2	1
MoO ₃			1	<0.5	1			

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APPENDIX B

**RADIOACTIVITY OF ACTINIDE, FISSION PRODUCT, AND ACTIVATION
PRODUCT RADIONUCLIDES IN WASTE GLASS**

This appendix shows the radioactivity associated with significant radionuclides in DWPF glass at selected times.

Note: (1) Nuclides contributing <0.0010% are omitted. (2) Basis is one canister (i.e., 1682 kg) of sludge plus precipitate glass. (3) The reference time is the time at which the waste is immobilized which, for this appendix, was assumed to occur in 1994.

Source: Characteristics of Potential Repository Wastes, DOE Report IRW-0184-RI, Vol. 3, July 1992.

Table B-1. Radioactivity of Fission Products in DWPF HLW

Nuclide	Curies					
	1 y	10 y	100 y	1000 y	10,000 y	100,000 y
Se-79	1.700E-01	1.700E-01	1.698E-01	1.682E-01	1.528E-01	5.848E-02
Sr-90	4.565E+04	3.685E+04	4.326E+03	2.151E-06	0.0	0.0
Y-90	4.566E+04	3.686E+04	4.327E+03	2.152E-06	0.0	0.0
Zr-93	1.117E+00	1.117E+00	1.117E+00	1.116E+00	1.112E+00	1.067E+00
Nb-93m	5.272E-02	4.236E-01	1.054E+00	1.061E+00	1.056E+00	1.014E+00
Nb-94	9.647E-05	9.644E-05	9.614E-05	9.323E-05	6.857E-05	3.173E-06
Tc-99	3.080E+00	3.080E+00	3.079E+00	3.070E+00	2.981E+00	2.224E+00
Ru-106	1.132E+03	2.324E+00	0.0	0.0	0.0	0.0
Rh-106	1.132E+03	2.324E+00	0.0	0.0	0.0	0.0
Pd-107	1.473E-02	1.473E-02	1.473E-02	1.473E-02	1.472E-02	1.457E-02
Sb-125	6.616E+02	6.958E+01	1.151E-08	0.0	0.0	0.0
Te-125m	1.623E+02	1.698E+01	2.809E-09	0.0	0.0	0.0
Sn-126	4.416E-01	4.416E-01	4.413E-01	4.386E-01	4.121E-01	2.208E-01
Sb-126	6.183E-02	6.182E-02	6.179E-02	6.140E-02	5.769E-02	3.092E-02
Sb-126m	4.416E-01	4.416E-01	4.413E-01	4.386E-01	4.121E-01	2.208E-01
Cs-134	2.410E+02	1.17E+01	6.453E-13	0.0	0.0	0.0
Cs-135	9.944E-02	9.944E-02	9.944E-02	9.941E-02	9.914E-02	9.649E-02

Table B-1 (Contd.)

Nuclide	Curies					
	1 y	10 y	100 y	1000 y	10,000 y	100,000 y
Cs-137	4.242E+04	3.446E+04	4.307E+03	4.009E-06	0.0	0.0
Ba-137m	4.013E+04	3.260E+04	4.074E+03	3.792E-06	0.0	0.0
Ce-144	4.051E+03	1.339E+00	0.0	0.0	0.0	0.0
Pr-144	4.051E+03	1.339E+00	0.0	0.0	0.0	0.0
Pr-144m	4.861E+01	1.606E-02	0.0	0.0	0.0	0.0
Pm-147	1.858E+04	1.723E+03	8.122E-08	0.0	0.0	0.0
Sm-151	2.460E+01	2.295E+02	1.147E+02	1.120E-01	0.0	0.0
Eu-152	3.506E+00	2.216E+00	2.257E-02	0.0	0.0	0.0
Eu-154	5.718E+02	2.768E+02	1.959E-01	0.0	0.0	0.0
Eu-155	4.131E-02	1.174E+02	4.042E-04	0.0	0.0	0.0
TOTAL	2.052E+05	1.432E+05	1.716E+04	6.580E-00	6.298E+00	4.948E+00

Table B-2. Radioactivity of Actinides and Daughters in DWPF HLW

Nuclide	Curies					
	1 y	10 y	100 y	1000 y	10,000 y	100,000 y
Tl-207	5.229E-11	4.778E-09	2.327E-07	3.418E-06	4.131E-05	4.467E-04
Tl-209	3.272E-12	3.645E-11	7.398E-10	6.245E-08	6.888E-06	1.531E-04
Pb-209	1.515E-10	1.688E-09	3.425E-08	2.891E-06	3.189E-04	7.087E-03
Pb-210	6.973E-13	8.359E-10	1.436E-06	7.680E-04	3.697E-02	2.901E-01
Pb-211	5.244E-11	4.791E-09	2.334E-07	3.428E-06	4.143E-05	4.480E-04
Pb-214	6.956E-11	9.353E-09	2.902E-06	7.682E-04	3.697E-02	2.902E-01
Bi-210	6.973E-13	8.359E-10	1.436E-06	7.680E-04	3.697E-02	2.901E-01
Bi-211	5.244E-11	4.791E-09	2.334E-07	3.428E-06	4.143E-05	4.480E-04
Bi-213	1.515E-10	1.688E-09	3.425E-08	2.891E-06	3.189E-04	7.087E-03
Bi-214	6.956E-11	9.353E-09	2.902E-06	7.682E-04	3.697E-02	2.902E-01
Po-210	2.250E-13	8.359E-10	1.436E-06	7.680E-04	3.697E-02	2.901E-01
Po-213	1.482E-10	1.651E-09	3.351E-08	2.829E-06	3.120E-04	6.933E-03
Po-214	6.955E-11	9.351E-09	2.902E-06	7.680E-04	3.697E-02	2.901E-01
Po-215	5.244E-11	4.791E-09	2.334E-07	3.428E-06	4.143E-05	4.480E-04
Po-218	6.958E-11	9.355E-09	2.903E-06	7.684E-04	3.698E-02	2.902E-01
At-217	1.515E-10	1.688E-09	3.425E-08	2.891E-06	3.189E-04	7.087E-03

Table B-2 (Contd.)

Nuclide	Curies					
	1 y	10 y	100 y	1000 y	10,000 y	100,000 y
Rn-219	5.244E-11	4.791E-09	2.334E-07	3.428E-06	4.143E-05	4.480E-04
Rn-222	6.958E-11	9.355E-09	2.903E-06	7.684E-04	3.698E-02	2.902E-01
Fr-221	1.515E-10	1.688E-09	3.425E-08	2.891E-06	3.189E-04	7.087E-03
Ra-223	5.244E-11	4.791E-09	2.334E-07	3.428E-06	4.143E-05	4.480E-04
Ra-225	1.515E-10	1.688E-09	3.425E-08	2.891E-06	3.189E-04	7.087E-03
Ra-226	6.958E-11	9.355E-09	2.903E-06	7.684E-04	3.698E-02	2.902E-01
Ac-225	1.515E-10	1.688E-09	3.425E-08	2.891E-06	3.189E-04	7.087E-03
Ac-227	5.244E-11	4.789E-09	2.333E-07	3.428E-06	4.143E-05	4.480E-04
Th-227	5.172E-11	4.725E-09	2.302E-07	3.381E-06	4.085E-05	4.418E-04
Th-229	1.515E-10	1.688E-09	3.425E-08	2.891E-06	3.189E-04	7.087E-03
Th-230	3.275E-07	4.931E-06	1.788E-04	4.473E-03	4.758E-02	2.877E-01
Th-231	1.574E-04	1.575E-04	1.587E-04	1.699E-04	2.679E-04	5.740E-04
Th-232	5.563E-14	5.569E-13	4.627E-12	6.194E-11	1.030E-09	1.674E-08
Th-234	1.050E-02	1.050E-02	1.050E-02	1.050E-02	1.050E-02	1.050E-02
Pa-231	3.329E-09	3.335E-08	3.340E-07	3.427E-06	4.142E-05	4.479E-04
Pa-233	8.911E-03	8.979E-03	1.057E-02	1.958E-02	2.230E-02	2.166E-02

Table B-2 (Contd.)

Nuclide	Curies					
	1 y	10 y	100 y	1000 y	10,000 y	100,000 y
Pa-234m	1.050E-02	1.050E-02	1.050E-02	1.050E-02	1.050E-02	1.050E-02
Pa-234	1.365E-05	1.365E-05	1.365E-05	1.365E-05	1.365E-05	1.365E-05
U-233	1.623E-06	1.983E-06	5.812E-06	6.913E-05	9.209E-04	7.765E-03
U-234	3.848E-02	7.475E-02	3.251E-01	5.654E-01	5.516E-01	4.297E-01
U-235	1.574E-04	1.575E-04	1.587E-04	1.699E-04	2.679E-04	5.740E-04
U-236	1.128E-03	1.130E-03	1.154E-03	1.379E-03	2.766E-03	3.625E-03
U-237	3.903E-02	2.531E-02	3.324E-04	1.819E-10	7.291E-11	4.731E-14
U-238	1.050E-02	1.050E-02	1.050E-02	1.050E-02	1.050E-02	1.050E-02
Np-237	8.911E-03	8.979E-03	1.057E-02	1.958E-02	2.230E-02	2.166E-02
Np-239	5.787E-03	5.782E-03	5.733E-03	5.269E-03	2.263E-03	4.829E-07
Pu-236	9.575E-02	1.074E-02	1.572E-09	1.560E-09	1.477E-09	8.588E-10
Pu-238	1.473E+03	1.372E+03	6.737E+02	5.507E-01	0.0	0.0
Pu-239	1.291E+01	1.291E+01	1.287E+01	1.254E+01	9.680E+00	7.245E-01
Pu-240	8.693E+00	8.768E+00	8.880E+00	8.078E+00	3.111E+00	2.228E-04
Pu-241	1.591E+03	1.032E+03	1.355E+01	6.200E-06	2.976E-06	1.931E-09
Pu-242	1.225E-02	1.225E-02	1.224E-02	1.222E-02	1.203E-02	1.024E-02

Table B-2 (Contd.)

Nuclide	Curies					
	1 y	10 y	100 y	1000 y	10,000 y	100,000 y
Am-241	1.362E+01	3.191E+01	5.793E+01	1.379E+01	1.042E-05	1.931E-09
Am-242m	1.440E-02	1.382E-02	9.169E-03	1.514E-04	0.0	0.0
Am-242	1.433E-02	1.375E-02	9.124E-03	1.506E-04	0.0	0.0
Am-243	5.787E-03	5.782E-03	5.733E-03	5.269E-03	2.263E-03	4.829E-07
Cm-242	1.675E-02	1.138E-02	7.545E-03	1.246E-04	0.0	0.0
Cm-244	1.035E+02	7.336E-01	2.341E+00	2.575E-15	0.0	0.0
SUM	3.203E+03	2.531E+03	7.697E+02	3.564E+01	1.382E+01	4.212E+00
TOTAL	3.203E+03	2.531E+03	7.697E+02	3.564E+01	1.382E+01	4.212E+00