2 of 3

United States Department of Energy

Office of Waste Management

HIGH-LEVEL WASTE BOROSILICATE GLASS

A COMPENDIUM OF CORROSION CHARACTERISTICS

VOLUME 2

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

MASTER

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

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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 μm
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.)

exfoliation:	for this document, "exfoliation" involves the separation of a portion of the surface alteration layer from the underlying glass substrate; synonomous 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 (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 fist 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:	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
redox state:	general term referring to the reducing-oxidizing state of a medium
saturation rate:	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 oberved 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)
secondary phases:	solid materials produced by glass alteration
spallation:	breakoff, exfoliation, or detachment of surface layers from the glass substrate
speciation:	refers to the molecular and ionic forms of elements dissolved in aqueous solutions
steady state:	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)
Stern layer:	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

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	Alkali Borosilicate (Glass)
AES	Auger Electron Spectroscopy
ANL	Argonne National Laboratory
ASTM	American Society for Testing and Materials
AVH	Atelier Vitrification LaHague
AVM	Atelier Vitrification Marcoule
BDAT	Best Demonstrated Available Technology
CC	Complexant Concentrate
CFR	Code of Federal Regulations
CVS	Composition Variability Study
DIW	Deionized Water
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EBS	Engineered Barrier System
EDS	Energy Dispersive X-Ray Spectroscopy
EELS	Electron Energy Loss Spectrometer
EMP	Electron Microprobe analysis (sometimes EMA Electron Microprobe Analysis)
EPA	U.S. Environmental Protection Agency
ESCA	Electron Spectroscopy for Chemical Analysis
FEH	Free Energy of Hydration (Model)
FTIR	Fourier Transform Infrared
HLW	High-Level Waste
HLLW	High-Level Liquid Waste
HM	High Metal (aluminum)
HTGR	High-Temperature Gas-Cooled Reactor
HWVP	Hanford Waste Vitrification Plant
IAEA	International Atomic Energy Agency
ICP	Inductively Coupled Plasma
IRRS	Infrared Reflection Spectroscopy
ISO	International Organization for Standardization
JVF	Japanese Vitrification Facility
LFCM	Liquid-Fed Ceramic-Lined Melter
MCC	Materials Characterization Center
MFT	Melter Feed Tank
MIIT	Materials Interface Interaction Tests
NBO	Nonbridging Oxygen
NCAW	Neutralized Current Acid Waste
NCRW	Neutralized Cladding Removal Waste
NMR	Nuclear Magnetic Resonance
NRC	U.S. Nuclear Regulatory Commission
PBB	Permian Basin Brines

LIST OF ACRONYMS (Contd.)

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

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 II

1.0 INTRODUCTION

Glasses are metastable solids that undergo a number of corrosion processes when exposed to aqueous and/or humid air environments. In this document, the corrosion that occurs upon immersion in aqueous solutions is referred to as "aqueous corrosion" or simply "corrosion" processes. Corrosion that occurs in humid air or upon intermittent water contact is referred to as "weathering."

The extent of corrosion and the observed reaction products may be different for glasses reacted under different conditions. However, many of the same chemical reactions and physical processes occur under all conditions; differences in experimental observations are manifestations of differences in the relative rates of the same underlying processes. The overall glass corrosion kinetics and the nature of the end products can depend on the relative importance of individual processes and how they are coupled under different reaction conditions.

The principal heterogeneous chemical reactions involved in glass corrosion and weathering and the associated nomenclature are shown in Table 1-1. Homogeneous reactions, including nucleation and precipitation of secondary phases that occur after dissolution of glass components are too numerous to identify here. These corrosion reactions and solution reactions may be coupled (often through the solution phase). For example, the ion-exchange reaction (reaction 1 in Table 1-1) is coupled to network hydrolysis (reaction 4) and network dissolution (reaction 6) through the solution pH. Also, the network-dissolution reactions (6 and 7 in Table 1-1) are coupled to nucleation and precipitation of secondary Si phases through the aqueous silicic acid concentration (see Volume II,[1] Section 2.3). In addition, the rate of the overall corrosion reaction may be influenced or determined by physical processes that influence the rate of mass transport of reactants and products, including molecular diffusion, cracking, and spallation or exfoliation of surface layers.

Borosilicate glass alteration in near-neutral to alkaline solutions is initiated through ion exchange and hydration of the glass network. After the initial development of a diffusion layer, the rate of the overall corrosion process appears to be controlled, under most circumstances, by dissolution of the glass network at the outermost surface of the diffusion layer (see Volume I, Section 3). Precipitates form at the interface with contacting water when it becomes supersaturated with respect to secondary alteration phases. Together with the gel layer and the diffusion/ion-exchange layer, these precipitates constitute the surface alteration layers. The surface layers (see Section 2.1.1) can be considered to represent progressive stages in the alteration of the glass. Close to the interface with the unaltered glass, the glass is altered only as a result of ion exchange and interdiffusion of the exchanging species. Water diffusion has been observed to have progressed farther into the glass than dealkalization under some conditions. Water diffusion alone without release of alkali elements or boron results in minimal disruption of the glass network.

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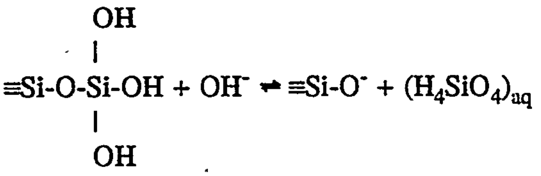
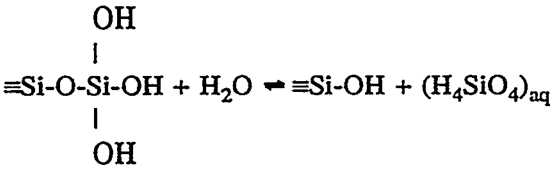
[1] Note: Unless otherwise stated, each section citation is understood to refer to a section in this Volume II.

Table 1-1. Reactions Contributing to Waste Glass Corrosion

	Reaction	Nomenclature
1	$\equiv Si\text{-}O\text{-}Na + H_3O^+ \rightleftharpoons \equiv Si\text{-}OH + Na^+ + H_2O$	Ion exchange
2	$2\equiv Si\text{-}O\text{-}Na + H_2O \rightleftharpoons 2\equiv Si\text{-}OH + Na_2O$	Hydrolysis reactions at nonbridging oxygen sites
3	$\equiv Si\text{-}O\text{-}Na + H_2O \rightleftharpoons \equiv Si\text{-}OH + Na^+ + OH^-$	
4	$\equiv Si\text{-}O\text{-}Si\equiv + OH^- \rightleftharpoons \equiv SiOH + \equiv Si\text{-}O^-$	Network hydrolysis (forward reaction)
5	$\equiv Si\text{-}O\text{-}Si\equiv + H_2O \rightleftharpoons \equiv SiOH + \equiv Si\text{-}OH$	Condensation (reverse reaction)
6	 $\equiv Si\text{-}O\text{-}\overset{OH}{\underset{OH}{\overset{\vert}{\underset{\vert}{Si}}}}\text{-}OH + OH^- \rightleftharpoons \equiv Si\text{-}O^- + (H_4SiO_4)_{aq}$	Network dissolution (forward reaction)
7	 $\equiv Si\text{-}O\text{-}\overset{OH}{\underset{OH}{\overset{\vert}{\underset{\vert}{Si}}}}\text{-}OH + H_2O \rightleftharpoons \equiv Si\text{-}OH + (H_4SiO_4)_{aq}$	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].

While all processes mentioned above may occur simultaneously, glass corrosion is usually dominated by the effects of one or two processes, although the dominant processes may change as corrosion progresses. Dealkalization is considered to be the dominant corrosion process during the initial glass-water interaction. As the pH increases, ion-exchange reactions slow and the network-dissolution reactions dominate the glass corrosion [STRACHAN-1990; BOURCIER-1991]. As the solution becomes more concentrated, the dissolution reactions also become slow. Recently reported work by Grambow et al. [GRAMBOW-1992a] on the reaction of R7T7 glass in brines, by Van Iseghem et al. [VAN ISEGHEM-1992] on five Al-rich waste glasses in deionized water, and by Lemmens and Van Iseghem [LEMMENS-1992] on SM527 glass in deionized water and clay water suggest that the long-term glass corrosion rate becomes diffusion-controlled. Grambow et al. suggest that water diffusion becomes rate-controlling in the long-term, while Van Iseghem et al. [VAN ISEGHEM-1992] suggest that the ion-exchange reaction between H_3O^+ and Na^+/Li^+, rather than diffusion of H_2O, is the rate-controlling process. Grambow [GRAMBOW-1987] showed that network hydrolysis may follow a square root of time dependence, if silica transport through a surface layer is rate-limiting. Grambow et al. [GRAMBOW-1992a] further pointed out that the rate-limiting step might change if the test conditions are changed. More work is needed to identify the rate-controlling process relevant to long-term corrosion [GRAMBOW-1991; VAN ISEGHEM-1992].

This volume summarizes experimental observations related to waste glass corrosion and weathering. Techniques for characterizing surface layers are discussed in Section 1.1. The practical experimental measures of waste glass corrosion are discussed in Section 1.2. Testing methods and parameters are discussed in Sections 1.3 and 1.4. Section 2 discusses the effects of various parameters on waste glass corrosion, and waste glass weathering is discussed in Section 3. Glass corrosion effects due to interactions with other materials that may be present in a geologic repository and field testing results are discussed in Section 4. Section 5 discusses results obtained from studies of the corrosion of natural glasses of great age.

1.1 Techniques for Characterizing Surface Layers

Important characteristics of the surface layers include compositional profiles, identity of crystalline phases that form (especially those bearing actinides), morphology and micromorphology of the layers, and oxidation states of multivalent components. Glass corrosion is often slow and invariably results in products that are inhomogeneous on a very small scale. Several sophisticated analytical techniques are required to understand the reaction processes. The methods that have been applied to the study of reacted glass layers are discussed in this section, along with some of their limitations. Relating data from several techniques requires an understanding of these limitations. For example, many techniques require the sample to be analyzed under vacuum. This may result in the partial dehydration of phases which comprise the surface layer. Local heating of the sample during analysis may also cause dehydration of the probed region.

In general, the experimental methods rely on the interaction of a probe with the solid sample. The sample-probe interaction generates a signal that is detected and used to characterize the sample. Within this general framework are many experimental limitations. The probe-sample interaction may be spatially nonspecific, and it may be accompanied by other undesired and yet unavoidable interactions. Such interactions are particularly true of complicated glasses and many of their reaction products, which are good insulators. Also, artifacts can be associated with coupling the signal to the detector, and detectors have background and resolution limitations that must be considered.

Analytical techniques that use the same probe or the same detector can be expected to share many of the same limitations. Several techniques make use of ion beams to sputter away the surface of the reacted glass. Some of the atoms removed from the surface by this ion-milling process are ionized. In secondary ion mass spectrometry (SIMS), these ions are mass analyzed to determine the atomic make-up of the material removed by the ion-milling process [MAGEE-1978; CLARK-1979; McVAY-1980a; JSS-1984; LODDING-1985; WILSON-1989; VERNAZ-1989; OVERSBY-1992a]. When the sputtering rate is carefully calibrated, these data can be expressed as concentration profiles. Electron spectroscopy for chemical analysis (ESCA) [PEDERSON-1981], X-ray photoemission spectroscopy (XPS), and Auger electron spectroscopy (AES) [CLARK-1979] detect low-energy electrons emitted from the surface of a specimen in response to different stimuli. Because these electrons can penetrate only a few angstroms of material, such techniques provide information about only the outermost surface. To generate a depth profile, ion-beam sputtering is used to remove successive layers from the surface; data are collected from the exposed surface and assembled into a depth profile. Depth resolution depends on how precisely the sputtering rate can be determined; it is typically about 10 nm for single-component materials and higher in multilayer samples where sputtering rates can vary from layer to layer [ZIEGLER-1978].

All of these techniques share problems associated with the nonspecific nature of the ion-milling process because more than one process occurs in real systems. Ion-beam mixing can occur in the subsurface region due to dislocation cascades initiated by the incident ions. Preferential sputtering can occur because some elements are more easily sputtered than others. These effects result in apparent compositional variations being measured. Sputtering of insulators can also result in charging effects (which can be partially compensated by simultaneously flooding the sample with electrons), and these effects cause variations in detector collection efficiency. The SIMS technique is also sensitive to the fact that the number of species ionized in the sputtering process is dependent on the matrix being sputtered, so apparent compositional variations are possible.

Rutherford backscattering (RBS) and resonance nuclear reaction analysis (RNRA) make use of a high-energy ion beam to probe the sample [LANFORD-1977; PETIT-1990a]. Both techniques are based on the fact that ions lose energy as they penetrate a material. The deeper the penetration, the more energy is lost. In RBS analyses, backscattered ions are detected and used to generate concentration gradients; depth resolution is typically about 30 nm but can be better in optimized systems [WILLIAMS-1978]. In RNRA, the gamma ray generated by the nuclear reaction between a specific element in the sample and the incident ion is detected. The nuclear reaction is chosen to be one that occurs within a narrow energy range so the signal represents the concentration of the reactant at a certain depth. By increasing the incident beam energy, the ion beam reaches this energy at increasing depths in the solid and a depth profile can be generated. This technique has been particularly useful in producing hydrogen profiles, which are difficult to obtain with other techniques and are very important in understanding the leaching behavior of glasses [LANFORD-1976, -1978]. Sputtering and ion-beam mixing do not occur with this technique because the collision cross-section of ions in this energy range is much lower than that used in ion-milling. This method has a depth resolution of about 20 nm [ZIEGLER-1978].

Electron microscopy is a very versatile technique for studying corroded glasses. In scanning electron microscopy (SEM), an electron beam (<30 kV) is focused into a fine probe and rastered across the sample surface [GOLDSTEIN-1975]. A secondary signal is detected and used to generate an image synchronized with the raster scan of the sample; several secondary signals can be detected. Resolution of the images generated from each of the signals is limited by the probe size but depends as well on the contrast, the interaction volume of the beam and the solid generating the signal, and the efficiency of the signal detector. Low-energy secondary electrons are usually detected. Backscattered electrons, which are high-energy electrons from the main beam that are reflected from the sample in elastic collisions, can also be detected and used to form an image. Materials with high atomic numbers are more likely to reflect the high-energy electrons, so this sort of image enhances regions of the sample containing elements with high atomic numbers. Characteristic X-rays that are produced when the electron beam interacts with the sample can also be detected by either energy dispersive spectroscopy (EDS) or wavelength dispersive spectroscopy (WDS). The X-ray energies provide compositional information about the region of the sample where the probe is positioned. Electron microprobe analysis (EMA) is very similar to this mode of SEM operation; EMA is performed with a specialized instrument optimized for this application, although the distinction between EMA and SEM is fading in modern instruments. The surface morphology can be examined with SEM, or cross-sectioned samples can be examined to provide high magnification views of the reacted layers [BATES-1982a; CLARK-1979; VERNAZ-1989]. Ultimate resolution with SEM is limited by the size of the electron probe; however, for studies of glasses, which are good insulators, the need to coat the sample with a thin conductive layer and signal considerations are practical realities that actually limit resolution. Resolutions of about 1 μm are typical [VERNAZ-1989].

Transmission electron microscopy (TEM) forms an image using electrons transmitted through the sample [JOY-1986]. Although scanning transmission electron microscopy (STEM) is available, much of the work on waste glasses has been done in the "conventional" TEM mode. In this mode, the image is formed by focusing transmitted electrons with lenses that are shaped magnetic fields. The image resolution is limited by the wavelength of the electron and more practically by aberrations in the lenses to about 0.2 to 0.3 nm in modern instruments. With this resolution, a TEM can image lattice planes in clay crystallites (typically 0.7 to 1.5 nm). Although the interpretation is not straightforward, higher resolution studies of clays have been done [VEBLEN-1990]. Applications to waste glass surface studies have concentrated primarily on the measurement of basal spacings of clay crystallites [ABRAJANO-1990a]. In analytical electron microscopy (AEM), a transmission electron microscope is outfitted with an energy-dispersive X-ray spectrometer (EDS) and electron energy-loss spectrometers (EELS). The TEM can also be operated in a diffraction mode, and structural information can be obtained from very small regions. Thus, AEM can provide very high magnification images of reacted layers along with coupled compositional and structural information [EHRET-1986; VERNAZ-1989; ABRAJANO-1990a].

Charging effects may result from the interactions between incident electrons and the sample, and a buildup of electric charge may occur due to inadequate electric conductivity at the sample surface. This results in migration of alkali ions within the probed region and makes analysis very difficult [NIELSEN-1981; BANDO-1988]. This effect is very similar to one of the effects that limits SIMS analysis [WILSON-1989]. Localized heating of the probed region may also lead to migration.

The detector window most often used on an EDS is a Be window. The Be window is not transparent for characteristic X rays from elements with atomic numbers below Na and only modestly transparent for Na-characteristic X rays; minimum detection levels of about 0.5 wt.% are usually possible [GOLDSTEIN-1986] for most elements. Another process that limits the information available from TEM is dehydration of clays in the vacuum system of the microscope [TAZAKI-1990]; clay crystal lattice parameters can change when dehydrated.

Many methods probe the sample with electromagnetic radiation. Infrared reflection spectroscopy (IRRS) measures reflectance in the infrared region. In this spectral region, valence bands absorb, which provides information about the bonds that are present. This surface analytical technique samples a thickness of about a wavelength of light, 0.5 μm [CLARK-1979; JSS-1984]. Optical microscopy is used to inspect the morphology of samples and can be helpful in understanding the overall reaction process [VERNAZ-1991a]. It is particularly important when used in conjunction with higher resolution techniques to ensure that representative regions of samples are investigated.

X-ray diffraction (XRD) provides structural information through analysis of the diffraction of X rays as they penetrate a well-ordered crystal. Because most crystals produced by the reaction of glasses are extremely small, most XRD work has been powder diffraction. In this technique, an array of small crystallites with no particular preferred orientation produces a characteristic powder diffraction pattern that can be used as a "fingerprint" to quickly identify unknown phases. This powerful technique can provide accurate crystal spacings from a bulk (100 μm) sample [JSS-1984].

X rays are also absorbed as they pass through materials. At certain characteristic X-ray energies, a new excitation of the electrons in an atom becomes possible and the absorption cross-section increases suddenly. The structure at these absorption thresholds and the extended structure well beyond this threshold can convey a great deal of information about the local atomic ordering of the excited species [GREAVES-1990].

Many techniques have been applied to the study of waste glass reactions with water. Awareness of the limitations of the experimental techniques is essential to critically evaluate the data and to develop models based on that data. It is important, therefore, to make use of complementary techniques to piece together a comprehensive picture of glass corrosion. For example, although optical microscopy has considerably lower resolution than either SEM or TEM, it serves an important role in preliminary surveys of reactions and in selecting representative regions for analysis with electron microscopes. The spatial resolution of SIMS is less than that of SEM/EDS, which is less than that of TEM/EDS. However, SIMS is the more precise method for obtaining compositional information and TEM is the least precise. Thus, a complete characterization of corrosion products requires several techniques to be used in combination.

1.2 Experimental Measures of Waste Glass Corrosion

Contact of glass by a solution results in partial dissolution of the glass and alteration of the glass in contact with the solution. Although the extent of glass alteration is related strictly to the depth of water penetration, the penetration depth is difficult to measure. The observations that glass corrosion involves progressive alteration of the network ranging from water diffusion to dissolution, together with the effects of secondary phase precipitation on the measured leachate concentrations of species released from the corroding glass make it difficult to precisely define or operationally measure the extent of glass corrosion and weathering. The corrosion of waste glass is usually monitored experimentally by measuring the amounts of various glass components that have been released into solution or by measuring the thickness of the altered glass. Glass corrosion is best characterized by analyzing both the leachate and the altered solids. High-level radioactive waste (HLW) glasses generally contain many chemical components that have different solubilities and may be released from the glass at different rates (Section 2.2). Water diffusion into the glass and alkali depletion generally occur to a greater extent than network hydrolysis early in the reaction at low to moderate pH values, and an altered layer is generated at the glass surface (see Sections 2.1 and 2.3). The solution concentrations of the alkali metals, B, and Si are commonly used to indicate the extent of glass reaction [MENDEL-1984, Chapter 1]. Boron generally is released from nearly the same depth as the alkali metals [WICKS-1992; OVERSBY-1991, -1992a], even though B is usually identified as a network-forming component (see Section 2.2). Silicon is released primarily from the outer surface of the glass or altered layer, although, depending on the glass composition and test conditions, Si may be depleted in the altered layer as well. As the glass reacts and the leachate becomes more concentrated, secondary phases may precipitate from the leachate onto the glass surface or form colloidal particles that remain suspended in solution. Radioelements in solution also precipitate onto surfaces, form colloidal particles, or coprecipitate with secondary phases. The assemblage of secondary phases that form is expected to establish solubility limits for glass components in the leachate.

The solution concentrations of glass components that become incorporated into secondary phases no longer represent the amounts of those components released from the glass or the extent of glass reaction. Because B is incorporated into very few secondary phases, the solution concentration of B has been identified as best representing the extent of reaction [SCHEETZ-1985]. Boron release has also been shown to be sensitive to reaction conditions such as temperature, pH, and silicic acid concentration [PEDERSON-1983a; KNAUSS-1990; BOURCIER-1992], and it often provides the best available single measure of the extent of glass corrosion. In addition, B is rarely present in appreciable concentrations in repository components other than HLW glass so that the extent of glass corrosion can be measured in the presence of other repository component materials without the need for background corrections. In most laboratory tests, however, several glass components are monitored to provide a better characterization of the extent of reaction and the reaction mechanisms involved.

Under some test conditions, particularly in field tests, the leachate solution is not available for analysis, and the reacted glass must be analyzed to assess the extent of glass corrosion. Although analysis of the reacted glass cannot measure the amount of glass that has completely dissolved, the depletion depth of alkali metals and B (i.e., the alteration layer thickness) provides a useful measure of the extent of corrosion. Compositional and structural changes usually permit the layer to be clearly distinguished from the unreacted glass in a scanning electron microscope (SEM), and the layer thickness can be measured directly [HARKER-1987]. Also, the layers formed on monolithic samples may be mechanically removed and the weight loss of the specimen measured directly to determine the extent of corrosion.

1.3 Standardized Test Methods

Several different test methods have been used to characterize the chemical durabilities of HLW glasses. Standard test procedures have been developed to directly compare results obtained for different glass compositions. A summary of test methods used to measure the chemical durability of HLW glasses has been compiled by the International Atomic Energy Agency (IAEA) and is included in Table 1-2 [IAEA-1985, pp. 18-20]. These tests can be generally categorized as dynamic tests, in which the leachant is continuously or periodically refreshed; or as static tests, in which the leachant is not refreshed during the test. Commonly performed dynamic tests include the Materials Characterization Center (MCC) test MCC-4 [DOE-1981], Soxhlet tests, and replacement tests [ISO-1979]; static tests include the MCC-1 and MCC-3 tests [DOE-1981].

The MCC-1 test [DOE-1981] specifies that a monolithic glass specimen be used with deionized water, silicate water, or brine solution as the leachant. Although the sample size and leachant volume are not restricted, the glass surface area-to-solution volume (S/V) ratio is specified to be 10 m^{-1}. Reaction temperatures of 40, 70, or 90°C are used. Tests may be performed in radiation fields; however, if Teflon vessels are used, exposures are restricted to 1×10^5 R or less to minimize vessel interactions [STRACHAN-1983a]. Tests are run in a batch mode, wherein separate tests are performed for each test condition and reaction time to characterize the time-dependence of the reaction. Specific reaction times are recommended so the results of tests with different glass compositions can be compared directly. The MCC-1 test and modifications of the test have been used to generate an extensive database including the reactivities of various glass formulations produced worldwide [BIBLER-1984; STRACHAN-1983b; CANTALE-1991; HERMANSSON-1984; HARVEY-1982].

The MCC-3 test [DOE-1981] uses powdered glass to achieve a high S/V ratio. Leachates are more rapidly concentrated in tests performed at high S/V, and solution concentrations near saturation are achieved after short reaction times. The vessel is continuously agitated during the test. A test similar to the MCC-3, the Product Consistency Test (PCT), has been developed by Westinghouse Savannah River Company. The PCT is performed under static conditions with crushed glass (-100+200 mesh fraction) in deionized water at 90°C [JANTZEN-1992a]. The glass mass/leachant volume ratio specified in the test is 1 g of crushed glass per 10 mL of water, which corresponds to an S/V of about 2000 m^{-1}. The extent of reaction is measured using the solution concentrations of released glass components, as in the MCC-1 and MCC-3 tests.

Table 1-2. Summary of Leach Test Methods. Modified from [IAEA-1985, pp. 18-20]

Name of Test	Temp. (°C)	Leachant	Flow Rate	Sample Description	Ref.
Soxhlet	50-100	Distilled water	1.5 cm^3/min	Plate, $S = 3\ cm^2$	[1]
Modified Soxhlet	35-100	Distilled water	Variable	Grains or plate S = Variable	[2]
Hot-Cell Soxhlet	100	Distilled water	80 cm^3/h	Beads/plates/chips S = Variable	[3]
MCC-5 Soxhlet	100	Distilled water	~1.5 cm^3/min	Plate, $S = 4\ cm^2$	[4]
Soxhlet (PNC)	70,100	Distilled water	60-225 cm^3/h	Bar, $S = 2\ cm^2$	[5]
HIPSOL (HT Soxhlet)	100-300	Distilled water	100-900 cm^3/h	Powder or block	[6]
IAEA	25	Distilled water	Periodic replacement	Cylinder with exposed surfaces	[7]
ISO Buffer	23-100	Distilled water, buffers, and sea water	Periodic replacement	Monoliths	[7]
Powder (P1)	95-200	Distilled water	Periodic replacement	Powder, 100-200 μm	[8]
Powder (P2)	40-100	Deionized water	Daily replacement	Powder, 100-150 mesh	[9]
MCC-4	40,70,90	Distilled and reference groundwater	0.1 - 0.001 cm^3/min	Plate, $S = 4\ cm^2$	[4]
Low Flow	25-90	Distilled water	1 cm^3/wk	Plate, $S = 3\ cm^2$ (radiotracers)	[10]
Dynamic	35-90	Distilled water	3-1200 cm^3/h	Grains or monoliths	[11]
Grain Titration	100	Distilled water	Static	Powder	[12]
Time-Dependent Method	20-~60	Buffered water	Static	Disc	[10]
MCC-1	40,70,90	Distilled and reference groundwater	Static	Monolith $S/V = 10\ m^{-1}$	[4]
MCC-2	110,150, 190	Distilled and reference groundwater	Static	Monolith $S/V = 10\ m^{-1}$	[4]
MCC-3	40,90,110, 150,190	Distilled and reference groundwater	Static (agitated)	Crushed (1) 149-175 μm (2) <45 μm	[4]

Table 1-2 (Contd.)

Name of Test	Temp. (°C)	Leachant	Flow Rate	Sample Description	Ref.
HTLT (CEC)	90,110,150, 190	Distilled water	Static	$S = 4\ cm^2$	[13]
Autoclave (HMI)	150-200	Distilled water and brines	Static	Beads, chips	[14]
Autoclave (KfK)	100,150, 200,250	Distilled water and brines	Static	Cylinders $S = 20$ or $5\ cm^2$	[15]
Repository Simulation	25-90	Granite equilibrated water	None (sampling equivalent to $1\ cm^3$/month)	Plate $S = 3\ cm^2$	[10]
Waste/Water/ Rock Leach	98	Distilled or granite water		Glass cube: $S = 6\ cm^2$ 20 g granite powder: 250-710 μm, $60\ cm^2$ water	[5]
MCC-14	25-250	Repository groundwaters	Static or periodic sampling	Monoliths and powders	[4]
PCT	90	Deionized water	Static	Crushed 74-149 μm	[16]

[1] H. Nakamura and S. Toshiro, Progress Report on Safety Research of High-Level Waste Management for the Period April 1982 to March 1983, Japan Atomic Energy Research Institute Report JAERI-M-83-076 (1983).

[2] M. Hussain and L. Kahl, "Incorporation of Precipitation from Treatment of Medium-Level Liquid Radioactive Waste in Glass Matrix or Ceramics Together with High-Level Waste," Ceram. in Nucl. Waste Manag. Proc. Int. Symp (1979).

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[16] C. M. Jantzen, N. E. Bibler, D. C. Beam, W. G. Ramsey, and B. J. Waters, Nuclear Waste Glass Product Consistency Test (PCT) Version 5.0(U), Westinghouse Savannah River Co. Report WSRC-TC-90-539, Rev.2(1992).

The MCC has recommended that the solution results be expressed in terms of normalized elemental release, which is simply the measured concentration of a glass component in solution, in g/m^3, divided by the S/V of the test, in m^{-1}, and divided by the weight fraction of that component in the unreacted glass [DOE-1981]. The normalized elemental mass loss is then given in units of g/m^2 and the normalized release rate in $g/m^2/d$. This function accounts for the effects of different glass compositions and different S/V ratios on the solution concentration, so test results can be compared directly using the normalized elemental release values. The effects of glass composition and S/V ratio on the glass reaction are discussed in Sections 2.2.4 and 2.3.1, respectively.

Dynamic tests are performed with either continuous or periodic refreshment of the leachant and removal of leachate from the system throughout the test period. The removal of reaction products affects the glass reaction rate (see Section 2.3.2). In Soxhlet tests, leachant is continuously boiled, condensed, and dripped into a sample container where the reaction occurs. The leachate overflows the sample container and returns to the leachant source as fresh leachant is added to the sample container (see [DELAGE-1991] for a more detailed description of a Soxhlet device). Glass reaction products become concentrated in the distillant solution throughout the test duration. Different reaction temperatures near the leachant boiling point can be tested by varying the pressure in the apparatus.

Single-pass, continuous-flow tests--such as the MCC-4 low-flow-rate method [DOE-1981]--utilize peristaltic pumps to vary the flow rate of leachant through a cell containing the glass sample(s). The cell may be placed in an oven to assess thermal effects on the glass reaction. Dynamic tests allow monitoring of the leachate throughout the test period and analysis of the effects of the flow rate and leachant composition.

The very low flow rates expected in repositories worldwide cannot be conveniently attained in continuous-flow apparatus, and they are usually simulated by using periodic replacement tests. Replacement tests require the periodic removal of leachate and replacement by an equal volume of fresh leachant during the test period. Replacement frequency and volumes vary among different test protocols. The replacement test designated by the International Organization for Standardization (ISO), as used at the Hahn-Meitner-Institute [ISO-1979], replaces the entire volume daily for the first five days, every third day for four replacements, every seven days for four replacements, and monthly thereafter [IAEA-1985, pg. 25]. Other replacement tests use replacement volumes that are a small fraction of the total volume [BARKATT-1981a]. The Soxhlet tests described earlier are, in effect, replacement tests because leachant is added to the sample container and leachate drips periodically from the sample container to remove reaction products.

Dynamic tests have been used to assess glass reactivity at different temperatures [DELAGE-1991; KNAUSS-1990], in different leachant solutions [KNAUSS-1990; BOURCIER-1992], and at different flow rates [ADIGA-1985; BARKATT-1984a]. At high flow rates, the buildup of dissolved components is minimized and the intrinsic reactivity of the glass can be characterized. At low flow rates, the glass reactivity is strongly affected by the buildup of dissolved glass components in the leachate (see Volume I, Section 3.2).

1.4 Testing Parameters

The key experimental testing variables discussed in this compendium are those that have been identified as parameters or test conditions specified in standardized testing methods. For example, the MCC-1 test has identified temperature, S/V ratio, leachate composition, and testing time as testing parameters for which values are specified in the method. The set of key experimental variables identified as potentially important also includes the composition of the waste glass (including elemental composition, presence of crystalline phases, and homogeneity), the leachant composition, pH, Eh, flow or refreshment rate, radiation, and the presence of other materials--including engineering materials such as iron and bentonite clay [McVAY-1983; IAEA-1985, pp. 144-151; HERMANSSON-1985]. Although it is recognized that few tests measure the separate effects of individual variables during the course of experimental testing, it is convenient to organize discussion of the experimental results by considering first the separate effects of key parameters (see Sections 2.1 through 2.5) and then the combined effects (see Sections 4.1 and 4.2). More specifically, Sections 2.1 to 2.6 address the effects of reacted layers, glass composition, solution composition, S/V ratio, flow rates, temperature, radiation, and microbes on glass corrosion. The effects of the solution chemistry are addressed throughout Section 2, and radionuclide release is discussed in Section 2.7. The effects of unsaturated conditions (i.e., conditions to which waste glass might be exposed in a geologic repository when the excavated openings, fractures, and pores in the hot rock are not filled with groundwater) are addressed in a separate section, Section 3. The effects of materials interactions are discussed in Section 4.2, although some of the effects of materials interactions are also addressed in Sections 2.1 through 2.5.

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2.0 WASTE GLASS CORROSION

Waste glass corrosion is affected by surface alteration layers on the glass surface, glass composition, S/V ratio, temperature, and radioactive decay. The effects of these parameters are discussed in Sections 2.1 through 2.5.

2.1 Characteristics and Effects of Surface Layers

The corrosion rate of waste glass may be influenced by mass transport through the surface layers, and through the effects of the surface layers on the solution chemistry. Radionuclides may be retained in the surface layers, or may be carried into solution as surface layers spall from the glass and form colloids. This section reviews the formation of surface layers (Section 2.1.1), the nature of surface layers (Section 2.1.2), and the role they play in the long-term corrosion of waste glass (Section 2.1.3).

2.1.1 Formation of Surface Layers during Glass Corrosion

When in contact with an aqueous solution and/or humid air environment, a HLW glass is subject to chemical attack that results in progressive alteration of the glass matrix. Constituent elements of the glass pass into solution, elements initially in solution diffuse into or are adsorbed onto the solid and new phases appear. These processes lead to the formation of surface layers on corroded glasses. The understanding of glass corrosion and radionuclide release can be enhanced by investigating the development and nature of these surface layers. The typical structure observed in the surface layers of corroded glass is schematically shown in Fig. 2-1 [MENDEL-1984]. The surface layer consists of an outermost layer of material precipitated from solution, an innermost diffusion layer, and a "gel" layer that lies between the diffusion layer and the precipitated layer. The precipitated layer and the gel layer consist of both amorphous and crystalline phases. The diffusion layer, which is adjacent to the pristine glass, is partially hydrated and partially depleted of soluble elements (B, Li, and Na). The innermost part of the diffusion layer may consist of a region into which water has penetrated but which is not depleted in soluble elements. All these layers are referred to as surface layer(s); they differ structurally and/or compositionally from the original glass and are usually formed by more than one reaction process. The basic processes involved in the formation of surface layers include ion exchange, water diffusion, network hydrolysis and condensation, and precipitation. The roles these processes play in forming the surface layers are discussed in the Sections 2.1.1.1, 2.1.1.2, and 2.1.1.3.

2.1.1.1 Formation of the Diffusion Layer

Ion exchange (see reaction 1 in Table 1-1) occurs between a proton-bearing species, such as a water molecule and an alkali metal on a nonbridging oxygen site in glass [CHARLES-1959]. The ion-exchange process results in an increase in the leachate pH and generates a region in the glass that is depleted in alkali. In general, the ion-exchange process dominates glass alteration under acidic conditions [BUNKER-1983; ADVOCAT-1991; FENG-1991a]. For ion exchange to continue, water must diffuse into the glass to reach reaction sites and alkali metal ions must diffuse out of the glass. While water may diffuse into the glass without ion exchange occurring, ion exchange and water diffusion generally occur to similar depths. The rate-controlling step of the overall process has been

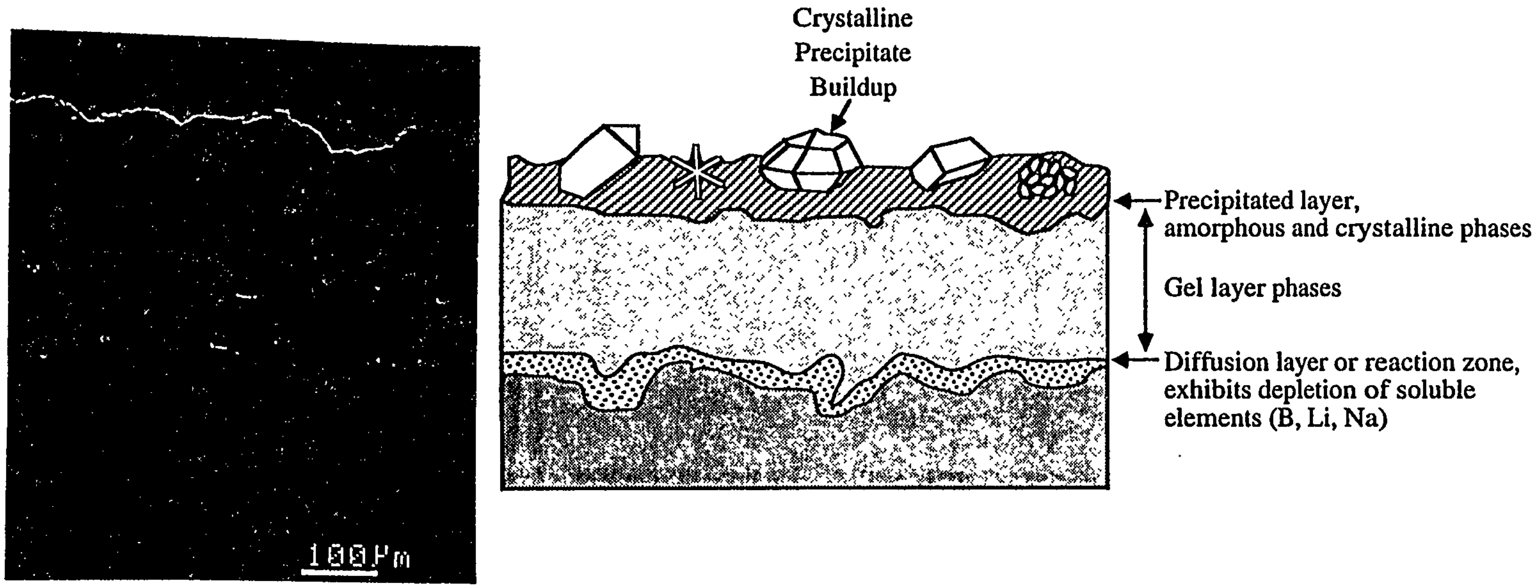


Fig. 2-1. Schematic of Surface Layer on Corroded Glass (adapated from [MENDEL-1984]). The photomicrograph shows the reacted layers on WVCM50 glass reacted for 10 days in saturated steam at 200°C (adapted from [EBERT-1991a]) (see Fig. 1-1 in Volume I).

identified to be interdiffusion of a proton-bearing species and alkali in simple glasses [DOREMUS-1975, -1983]. The diffusion of molecular water into HLW glass is followed by the more rapid release of alkali and hydroxide [SMETS-1982, -1983, -1984; BUNKER-1983, -1987].

The ratio of hydrogen in the layer to alkali removed from the layer has been utilized to determine whether molecular water or hydronium is the major infusing species. In simple glasses, H/Na ratios of 2.9 [LANFORD-1979] and 2.3 [PEDERSON-1986] have been measured. Dran et al. [DRAN-1989] reported a H/Na ratio of about 1 in the diffusion layer nearest the unreacted glass for both soda-lime-silicate glass and a simulated waste glass, a result they interpreted to indicate simple H^+/Na^+ exchange. Higher ratios were measured in the layer closer to the fluid. However, as pointed out by Schnatter et al. [SCHNATTER-1988], there are considerable experimental difficulties in measuring H/Na ratios in corroded glass due to outgassing of water from the alteration layers during measurement. The mechanism of alkali leaching and the dominant proton-bearing species may vary with test conditions [BUNKER-1983].

The rate of the dealkalization process is usually a linear function of the square root of time [SMETS-1982, -1983, -1984; BUNKER-1983, -1986, -1987; KUHN-1983; MENDEL-1984; FENG-1991a], and the growth of the surface layer thickness has a parabolic time dependence [SULLIVAN-1984; ABRAJANO-1989; TROTIGNON-1990a]. Corrosion experiments performed in deuterated water [SCHOLZE-1975, -1977; PEDERSON-1986, -1987; CASEY-1988; FENG-1991b] showed that glass corrosion rates were slower in deuterated water than in ordinary water under similar conditions. In leaching soda-lime-silicate glass, Pederson et al. [PEDERSON-1986] observed a D/Na replacement ratio of 2.3 ± 0.5 and an $^{18}O/D$ uptake ratio of 1.6 ± 0.3, which suggest hydrolysis and condensation reactions occur within the reaction zone (or diffusion layer) as the ion-exchange reaction proceeds. Pederson [PEDERSON-1987] later observed a consistent isotope effect during the leaching of a sodium silicate glass under constant pH conditions, both in the initial stage of Na release (which had leaching rate proportional to $time^{1/2}$) and in later stages (which showed leaching rate which was a linear function of time). Pederson [PEDERSON-1987] explained this result by suggesting that hydrolysis of the glass network is the rate-limiting step in both the $time^{1/2}$ and linear regimes and involves a proton transfer step in the hydrolysis of the silicate matrix. Matrix hydrolysis was also proposed as an important precursor to alkali release. Feng et al. [FENG-1991b] reported that the rate of corrosion of WV205 waste glass in D_2O was lower than the rate in H_2O by a factor that ranged between 1 and 3.6, depending on the test conditions (particularly S/V). A smaller isotope effect on the corrosion rate (1 to 1.4) was observed in the early stage of the glass reaction in tests performed at low S/V (<2000 m^{-1}). This was attributed to a diffusion-controlled corrosion process similar to that observed by Pederson [PEDERSON-1981]. However, a larger and variable isotope effect (up to 3.6) was observed in tests performed at high S/V which was attributed to a bond-breaking step involving H as the rate-determining step.

Ion exchange is strongly influenced by the concentrations of alkali and OH^- in solution [BUNKER-1983]. Feng and Pegg [FENG-1992a] showed that the addition of an alkali metal salt shifts the equilibrium of Reaction 1 in Table 1-1 to the left, which results in reduced glass leaching and lower leachate pH. The extent of the suppression of the ion-exchange reaction depends on the size and the mobility of the salt cations. Among alkali metal cations, Li^+ has the largest hydration energy, the largest hydration radius, highest hydration number, and lowest mobility. This implies that Li^+ in solution has the least capability to compete with hydronium ions to suppress the ion-exchange reaction. Feng and Pegg [FENG-1992a] reported the order of the alkali metal cations in suppressing the ion-exchange reaction to be $Li^+ < Na^+ < K^+ < Cs^+$. Lodding et al. [LODDING-1990] observed that the element depletion profile for SRL 165/TDS glass, leached in brine for two years, is in general, consistent with Feng and Pegg's results. Lodding found that Cs was depleted least and Li was depleted most in the diffusion layer. Feng and Pegg [FENG-1992a] demonstrated that the suppression of the ion exchange reactions by salt solutions is not due to the increased ionic strength of the solutions but is due to the shift of the ion-exchange equilibrium. Although the ion-exchange reaction rate may be decreased in saline or high pH solutions, the process may still occur at a low rate at pH $\geq$12 [EL-SHAMY-1972a; SMETS-1985] in saline solutions [LODDING-1990; FENG-1992a].

Water molecules must be present at the reaction site before the ion-exchange reaction can take place. Because the water diffusion rate is usually slower than the ion-exchange rate under normal test conditions, ion exchange and water diffusion usually occur to similar depths [BATES-1991a; MAZER-1992a]. However, water diffusion without accompanying dealkalization has been reported in natural obsidian [FRIEDMAN-1976; JEZEK-1978; AINES-1987; BATES-1988a] and in tektites [MAZER-1992b].

Water diffusion without dealkalization may also occur in concentrated alkali salt solutions. Dran et al. [DRAN-1989] observed H penetration deeper into glass than alkali depletion when they reacted a HLW glass at 200°C in 5 M NaCl solution. A water penetration rate of 0.42 $\mu m/d^{1/2}$ was observed by Dran et al., which is similar to the hydration rate of tektite, 0.39 $\mu m/d^{1/2}$, measured by Mazer et al. [MAZER-1992b] at the same temperature. Grambow et al. [GRAMBOW-1992a] reported a water diffusion controlled glass reaction rate of 0.3 $g/m^2/d^{1/2}$ (0.1 $\mu m/d^{1/2}$) at 90°C in salt solutions.

Vernaz et al. reported water penetration beyond the ion-exchange front for R7T7 glass leached under both dynamic and static test conditions at 100°C [VERNAZ-1991a]. Oversby and Phinney [OVERSBY-1992a] also reported H penetration to be greater than alkali depletion depths based on secondary ion mass spectrometry (SIMS) analysis of SRL 165 glass reacted under MCC-1 conditions at 90°C.

2.1.1.2 Formation of the Gel Layer

The corrosion of HLW glass is the result of several simultaneous and coupled processes (see Table 1-1) [HENCH-1986a; PEDERSON-1986; GRAMBOW-1990; BATES-1991a; BOURCIER-1991; ABRAJANO-1989; VERNAZ-1991b; JANTZEN-1992b]. For most waste glasses, the initial reaction that occurs is ion exchange. Hydroxide produced by ion-exchange reactions, together with hydroxide already in the leachant, promotes the hydrolysis reactions in the diffusion layer and also couples the ion-exchange and network-hydrolysis processes. Dissolution of the outer surface of the diffusion layer [LANFORD-1979; BARKATT-1981b; BUNKER-1987] transforms the outer part of the diffusion layer into a gel layer and limits the diffusion layer thickness to less than 1 μm [MENDEL-1984; VERNAZ-1991a]. Network-hydrolysis and condensation reactions may also lead to a restructuring and evolution of the gel layer [HENCH-1986a; PEDERSON-1986; VERNAZ-1992a]. It has been shown [KNAUSS-1990; VERNAZ-1991a] that thin surface layers are formed under high flow conditions at high pH where the glass corrosion rate is high. Thicker layers are formed at low pH and under static test conditions, where the glass corrosion rate is low due to the buildup of silicic acid concentration in solution (see Section 2.3.1). The stability of the gel layer is a strong function of solution composition. It incorporates less soluble species from solution [LEE-1985] and is depleted in elements which are highly soluble [LODDING-1990]. The layer thickness depends on the solubilities of individual elemental constituents of the glass. For example, the data of Knauss et al. [KNAUSS-1990] show that because of its low solubility, only Ca remains in the layer at alkaline pH. The commonly observed nonstoichiometric release of elements into solution may be due in part to limited solubilities and the incorporation of some elements into the surface layers [BOURCIER-1990; VERNAZ-1992a].

Hydrolysis of the silicate network is thought to occur via nucleophilic attack on a silicon atom (see reactions 4 and 5 in Table 1-1). Network hydrolysis is faster on a silicon atom with nonbridging oxygen (NBO) because the structural rearrangements required to form the 5-coordination intermediate become easier if the site is attached to the network by fewer bridging oxygens [BUNKER-1983]. This explains why increasing the alkali content in a glass, which results in an increase in NBO sites, usually decreases the durability of the glass. It also accounts for the observation that the addition of Al or B into a glass, which reduces the NBO sites by forming tetrahedral aluminate or borate sites, usually increases the short-term durability (see Section 2.2) [HENCH-1986a; FENG-1989].

2.1.1.3 Formation of the Precipitated Layer

As glass corrodes and releases elements to solution, the leachate may become saturated with respect to phases which precipitate onto the glass surface to form a precipitated layer. Precipitation may also occur due to singularities in the pH at locations not in equilibrium with the bulk solution [TROTIGNON-1990a; OVERSBY-1992a]. Such a local precipitation process may occur within the gel layer. Lee and Clark [LEE-1986] studied the surface layers formed on glass reacted in solutions containing NaCl, KCl, $MgCl_2$, $CaCl_2$, $ZnCl_2$, and $AlCl_3$. The compositions and properties of the surface layers varied considerably as the solution composition was changed. For example, the presence of Al ions in the $AlCl_3$ solution reduced the silica solubility by forming an insoluble aluminosilicate surface layer which reduced the glass dissolution rate. However, due to low pH of the $AlCl_3$ solution, waste glass continued to dissolve beneath this surface film and caused exfoliation of the aluminosilicate layer. Feng [FENG-1988a] reported a reduction in the glass dissolution rate of waste glass in a $Al(NO_3)_3$ solution at pH 7 due to the formation of a protective layer containing Al. Knauss et al. [KNAUSS-1990] demonstrated that the surface layer composition varied as solution pH was changed due to the pH dependence of phase solubilities. The surface layers formed when the glass was leached in pH 1 or pH 2 buffers did not contain Ca or Al because of the high solubilities of these elements at these pH values. Between pH 3 and 6, the surface layers contained Al and a small amount of Ca due to their reduced solubilities. At pH 11.8, aggregates of a fine-grained secondary mineral were found coating the glass surfaces. This observation is consistent with speciation/solubility calculations, which indicate saturation with respect to several Ca-silicate minerals. Grambow [GRAMBOW-1982] showed that the leachate compositions attained in tests with PNL 76-68 glass can be predicted by considering the solution to be in equilibrium with various metal hydroxides and carbonates. The composition of the precipitated surface layer could also be predicted as the glass corrosion progressed.

The leached surface of the waste glass becomes electrically charged due to the acid-base reactions between the glass surface and water [CASEY-1992a]. The net charge of a particular glass surface will be characteristic of its composition and structure. Nuclear waste glasses attain a negative charge in neutral and basic solutions due to dissociation of surface silanol groups. Once charged, oriented water molecules and counter-ions accumulate at the glass surface. The surface charge may promote sorption of positively charged metal ions, such as Ca^{2+} and Mg^{2+}, hydrolysis products, and colloids [LEE-1985]. Jantzen's [JANTZEN-1985a] zeta potential measurements of SRL 165 and SRL 131 glass over the pH range 4-10 indicate that the glass surface is strongly negative. Feng et al. [FENG-1993a] showed the colloids in SRL 131 leachates have a negative zeta potential over a pH range 1 to 11. The glass surface can also act as a nucleation center for precipitation [TROTIGNON-1990a]. Surface interactions are sensitive to the composition of the aqueous solution [LEE-1986; CASEY-1992a]. Ligands, cations, and anions in solution compete for surface sites. This competition introduces a complicated dependence of surface sorption on the solution chemistry.

2.1.2 Characteristics of Surface Layers

The general structure of the surface layers observed for HLW glasses shown schematically in Fig. 2-1 is well illustrated in Fig. 2-2, which shows a cross-section of WVCM50 glass reacted for 10 days in saturated steam at 200°C [EBERT-1991a]. A layer of precipitated phases about 100 μm thick has formed over a gel layer, which is about 200 μm thick. Analcime is the dominant mineral in the precipitated layer. The diffusion layer is not seen in this sample. Figure 2-3 shows precipitates formed on the surface of SRL 131 glass after reacting in water vapor at 202°C; it shows the formation of crystalline analcime and tobermorite, a Ca-Si phase, on the surface [BATES-1982a]. The TEM photomicrographs in Fig. 2-4 show the cross sections of the surface layers formed on SRL 165 glass after reacting in EJ-13 well water at 90°C [BATES-1991b]. The evolution of the surface layer with time illustrates how the surface layer structure can change with the reaction progress. The layer formed after 56 days is mostly amorphous and adheres to the underlying glass. After 91 days, the outer half of the layer has crystallized but the inner half remains amorphous. A dense "backbone" of amorphous iron, calcium, and zirconium has formed in the center of the layer. The entire layer has crystallized after 278 days. It is this layer that spalls or is detached from the glass under dynamic weathering conditions to form material that remains suspended in solution [WOODLAND-1991; BATES-1992a]. Other glasses have been found to develop more complex layers. For example, Abrajano et al. [ABRAJANO-1990b] observed at least six distinct layers formed on glass SRL 131 reacted at 90°C in deionized water for 546 days. Caurel et al. [CAUREL-1988] identified a 3 mm thick surface layer having seven sublayers on R7T7 glass after reaction at 300°C in deionized water at 50 m^{-1} for 28 days.

Surface layers formed during field tests often provide the only measure of the extent and mechanism of the reaction. (Field testing is discussed in Section 4.1). In the absence of leachate solutions, detailed analyses of the concentration profiles in the surface layers using SIMS and other surface techniques (see Section 1.1 for a discussion of these techniques) have provided insight into the alteration processes which occur during the corrosion of glass in field tests [LODDING-1985, -1992; WICKS-1992; HENCH-1984a, -1984b, -1986b].

The diffusion layer as shown in Fig. 2-1 is produced through the hydrogen and alkali ion-exchange reaction. The growth of this layer is controlled by the diffusion of water into the glass, but the growth is eventually limited by the outer side of the diffusion layer being converted to a gel layer (see below). The diffusion layer is the first alteration zone adjacent to the pristine glass. It has also been called the "glass reaction zone" by some researchers [MENDEL-1984; VERNAZ-1991a]. Concentration data for ions are obtained from surface methods such as SIMS [ABRAJANO-1988a], Auger electron spectroscopy, and nuclear reaction profiling [LANFORD-1979]. A typical concentration profile for Na^+ and H^+ is shown in Fig. 2-5. Note that the increased Ca content results from the inclusion of Ca from the leachant and residual Ca from the etched glass.

The diffusion layer is depleted in B [ROGGENDORF-1989; ZWICKY-1989; VERNAZ-1991a; OVERSBY-1992a]; the normalized leach rate for B from borosilicate glasses is similar to that of alkali [BUNKER-1986; LANZA-1988; FENG-1989; JANTZEN-1992b]. The HLW glasses usually have more alkali than the sum of acidic species such as B and Al [FENG-1988a, -1989] and the B in these glasses is usually tetrahedrally coordinated [BUNKER-1988]. However, for the R7T7 glass the acidic species are more abundant than the alkalis. Protonation of the NBO sites due to the ion-exchange reaction also catalyzes hydrolysis of adjacent borate bonds, resulting in leaching of alkali and B from the glass [BUNKER-1986]. The B-O-B and B-O-Si bonds are much less resistant to hydrolysis than

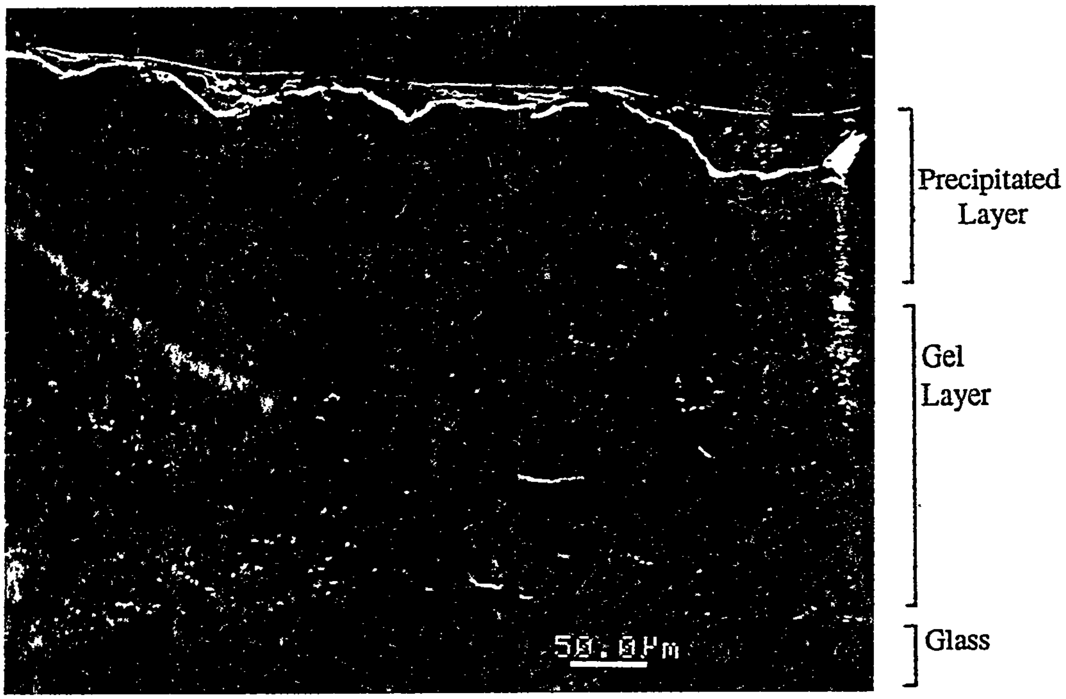
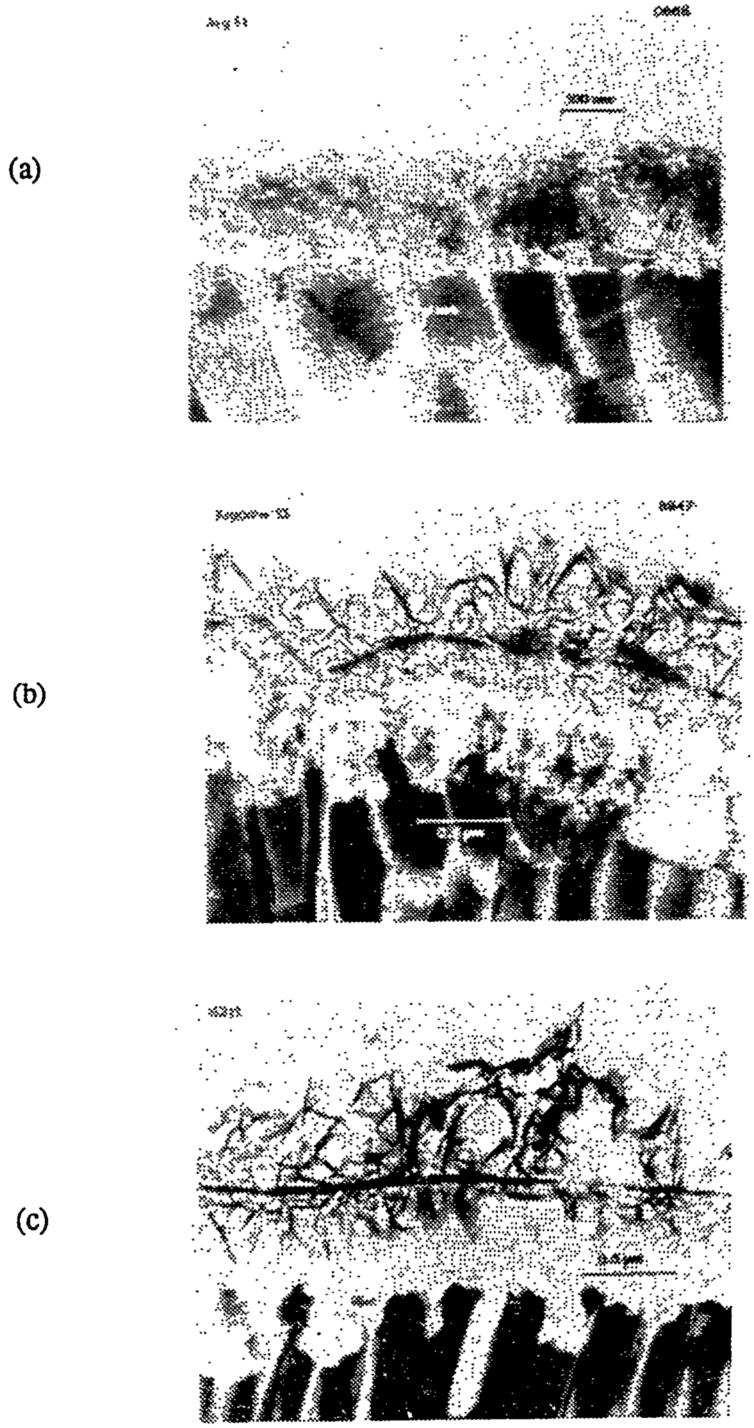


Fig. 2-2. Photomicrograph of Cross-Sectioned WVCM50 Glass Reacted for 10 Days in Saturated Steam at 200°C (adapted from [EBERT-1991a]).

Fig. 2-3. Some Minerals Formed on the Surface of HLW Glass (Type SRL 131) during Exposure to Water Vapor at 202°C (adapted from [BATES-1982a]).

Fig. 2-4. Brightfield Electron Micrographs of Cross-Sections of SRL 165 Glass Reacted in EJ-13 Water at 90°C at S/V = 30 m^{-1} for (a) 56 Days, (b) 91 Days, and (c) 278 Days (adapted from [BATES-1991b]).



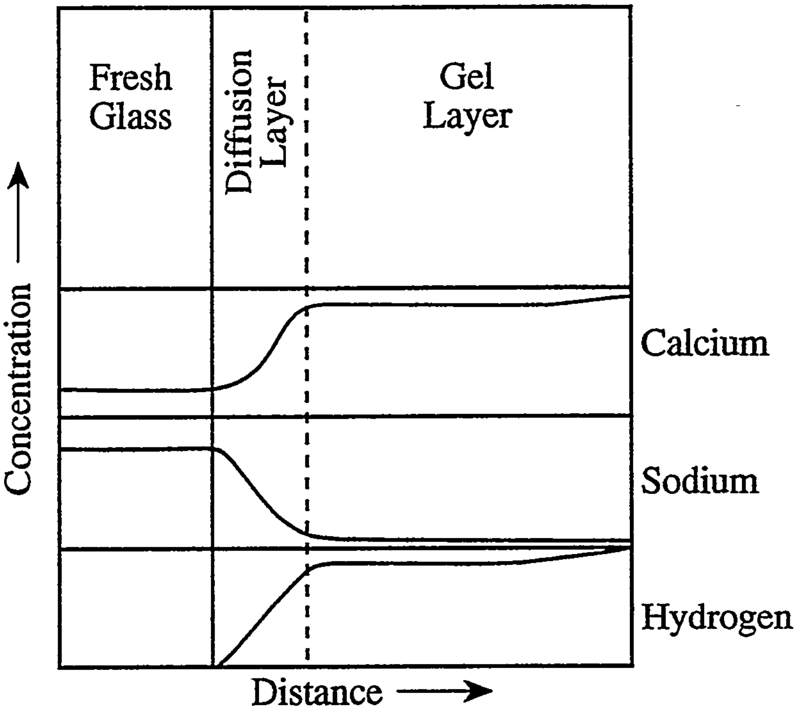


Fig. 2-5. Schematic of SIMS Profile for Polished Core Wafers of SRL 165U Glass Tested under Static Conditions in EJ-13 Water at S/V = 30 m^{-1} and 90°C (adapted from [BOURCIER-1990]).

Si-O-Si bonds [ILER-1979; BUNKER-1986]. The diffusion layer can also be depleted in alkaline earth elements under acidic conditions [KNAUSS-1990] because these ions are very soluble and are able to exchange with hydronium ions under acidic conditions. Thus, the composition of the diffusion layer also depends on the solution composition. The diffusion profiles for rare earth elements were studied by Scholze [SCHOLZE-1982].

The diffusion layer is formed by the leaching of soluble cations such as Na, B, and Li, leaving a skeletal structure of the network formers with the initial geometric dimensions [VERNAZ-1992a]. Formation of the diffusion layer is favored by acidic conditions. Advocat et al. [ADVOCAT-1991] reported that the diffusion layer formed on R7T7 glass at pH 4.8 is very similar in texture and morphology to unreacted glass. The depletion of certain soluble elements in the diffusion layer may be suppressed when the solution already contains a high concentration of those elements. For example, using the SIMS technique, Lodding et al. [LODDING-1990] found that only Li is significantly depleted in the diffusion layer formed after SRL 165 glass had reacted for 24 months in the Waste Isolation Pilot Plant (WIPP) in-situ test, a test which uses a brine having a high Na concentration.

The diffusion layer is usually very thin, less than 1 μm [MENDEL-1984; NOGUES-1985; VERNAZ-1991a], because the OH^- produced in the ion-exchange reaction promotes network-hydrolysis reactions that transform the diffusion layer into a gel layer. Vernaz et al. [VERNAZ-1991a] performed a systematic study of the diffusion layer developed on R7T7 glass and found that the diffusion layer was well defined and had a thickness of about 50 nm when R7T7 was tested under

Soxhlet conditions. Under static test conditions in a solution presaturated with glass components, the diffusion layer was less distinct from the bulk glass and had a thickness of about 100 nm. These observations are consistent with the general observation that, when the solution is saturated with glass components, it slows the hydrolysis reaction while the dealkalization reaction continues, resulting in increased thickness of the diffusion layer with time [BOURCIER-1991].

Pits are usually observed at the interface between the diffusion layer and the gel layer [MENDEL-1984; HARKER-1987; BANBA-1990; BATES-1992b]. The glass alteration advances as a uniform, moving front with local pitting [HARKER-1987]. Pitting phenomena are ubiquitous in the leaching of waste glass and have been shown to be enhanced by stress lines in the glass, phase separation, surface roughening, and microcracks [MENDEL-1984; BATES-1984a; FLINTOFF-1985; HENCH-1986a; HARKER-1987]. The pitting process causes the surface area of the glass exposed to the leach solution to increase with time.

The process of water diffusion into the glass matrix without dealkalization is generally not observed for HLW glasses under normal testing conditions because the rate of ion exchange is usually faster than water diffusion. However, Dran et al. [DRAN-1989] observed water penetration without alkali depletion when testing R7T7 waste glass at 200°C in 5 M NaCl; under these test conditions, the ion-exchange reaction was suppressed by the high concentration of Na^+ in solution. The hydrated region may be distinguished from bulk glass by the formation of a hydrated, brittle phase that is identifiable through birefringence in thin sections when viewed with an optical microscope [EWING-1979; BATES-1988a; MAZER-1992a].

The gel layer (Fig. 2-1) develops between the diffusion layer and the precipitated layer and usually accounts for the majority of the surface layer volume on a reacted glass [VERNAZ-1991a]. The gel layer is produced through hydrolysis and recondensation reactions, restructuring of hydration products, and migration of species [KNAUSS-1990; ABRAJANO-1990b; VERNAZ-1992a]. Evidence for the hydrolysis and recondensation reactions has been shown by the presence of ^{18}O [PEDERSON-1986] or ^{17}O [BUNKER-1988] from labeled leachant in the Si-O groups in the gel layer. The hydrolysis and recondensation reactions that result in the production and evolution of the gel layer are characterized by in-situ rearrangement of the hydrated species. In-situ formation of the gel is suggested by the fact that (1) the outer surface of the gel layer reproduces defects initially present in the pristine glass [MENDEL-1984; HARKER-1987; TROTIGNON-1990a]; (2) traces of fission tracks in the pristine glass are found in the gel layer after alteration [DRAN-1986]; (3) when small metallic particles (e.g., Pt, Zr, and Rh) or relatively insoluble crystals (such as spinels) are contained in the pristine glass, their distribution is unchanged in the gel layer [VERNAZ-1992a]; and (4) when glass beads, each containing different rare earths, are leached simultaneously in a single vessel, the gel layer around each bead contains only the rare earths initially present in that bead but none from the other beads [VERNAZ-1992a].

Oversby and Phinney [OVERSBY-1992a, -1992b] studied the structure of surface layers formed on SRL 165 glass (MCC-1, 90°C, in silicate solution) and suggested an orderly process for layer development--proceeding by penetration of molecular water into the glass, followed by migration of elements through the layer. During migration, the mobilized elements in the gel layer may form secondary phases that are controlled by local chemical conditions.

The growth of the gel layer may be indicative of the dominant glass reaction process. If the thickness of the gel layer increases as a linear function of the square root of time, a rate-controlling diffusion step is suggested [BATES-1983; SULLIVAN-1984; MANARA-1985; ABRAJANO-1989;

TROTIGNON-1990a]. A constant increase with time in the thickness of the gel layer has often been attributed to network hydrolysis being the rate-controlling process [ISHIGURO-1983; BUNKER-1987; ABRAJANO-1989; TROTIGNON-1990a]. The thickness of the gel layer is determined by a competition between the rate of dissolution of the gel layer at the water/gel layer interface and the rate of the gel layer generation at the diffusion layer/gel layer interface (see Fig. 2-1).

During long-term testing, the gel layer has been shown to evolve into more stable phases and repolymerize [LUTZE-1983; HAAKER-1985; ABRAJANO-1990b; BATES-1991a]. In Fig. 2-4a, the gel layer formed on SRL 165 glass reacting under static conditions for 56 days [BATES-1991b] is mostly amorphous and remains firmly attached to glass. After 91 days, a dual band structure becomes apparent and Fe has segregated into a well-defined "backbone" at the center (Fig. 2-4b). The backbone is also enriched in Ca and Zr. The surface layers include two layers separated by the backbone; the outer layer is composed of smectite clay plates, and the inner layer retains texture and composition characteristics similar to those of the 56-day sample. The inner layer appears to be starting to transform into smectite. The layers are now partially separated from the unreacted glass by a porous region that contains stringers of reacted glass. After 278 days, the banded structure is now mature, and smectite clay laths dominate both the inner and outer sides of the backbone (Fig. 2-4c).

The gel layers are usually porous [YASTREBOVA-1961; DOREMUS-1983; MENDEL-1984; BART-1985; TROTIGNON-1990b; VERNAZ-1992a] with a density between 0.8 and 2.5 g/cm^3, depending on glass composition and test conditions. Tests with flowing water produce the least dense surface layers whereas tests performed under high S/V or in silicate solutions produce the densest layers [VERNAZ-1992a]. Lanza and Parnisari [LANZA-1981] found that the surface layers formed on waste glass at high temperatures were more porous, contained less silica and more Fe, and were less protective than layers formed at lower temperatures. The pore size has been estimated to be about 0.3 nm using infrared spectroscopy [TROTIGNON-1990b], 1.5 to 2.5 nm using X-ray diffraction [VERNAZ-1992a], and 6 nm using gas adsorption [VERNAZ-1992a]. The gel layer generally shows a density gradient: the outer portion is less dense than the inner portion.

2.1.2.1 The Precipitated Layers

Precipitates are another major feature of surface layers on reacted waste glass. In static or low flow tests, where precipitation and complex formation is enhanced, the outer surfaces of the leached glasses contain a variety of structures that do not conform to the original geometry of the glass [MENDEL-1984]. Hench and Clark [HENCH-1986a] showed that under static test conditions the precipitated layer on SRL 131 glass is composed of colloid-sized particles. The precipitates can be amorphous or crystalline in nature, depending on the test conditions and the duration of the tests [ABRAJANO-1990b]. The precipitation of hydroxides, such as iron hydroxide (goethite), has been reported on waste glasses [PETIT-1989]. In leaching PNL 76-68 glass, Grambow [GRAMBOW-1982] modeled the leachate concentrations in tests with a waste glass as being in equilibrium with pure $Fe(OH)_3$ (amorphous), $Zn(OH)_2$ (amorphous), $Nd(OH)_3$, $SrCO_3$, or $CaCO_3$. Hench and Clark [HENCH-1986a] demonstrated that metal silicates were the dominant species precipitated on SRL 131 glass surfaces tested under static conditions, but the silica concentration in solution remained too low to generate metal silicates in high flow tests, and metal hydroxides were the dominant phases formed. A study by Petit et al. [PETIT-1989] showed that the formation of hydrosilicates or hydroxides depends on the glass reaction mechanism. For a congruent dissolution process, at the beginning of a test in which the Si concentration was low, highly hydrolyzable elements would tend to form hydroxides; subsequently, monomers of the released silicic acid would tend to adsorb on the hydroxides (such as Al, Fe, and Zn), which could then settle out of solution. This explains why the Si content in the gel layer has been observed to increase with time [VERNAZ-1991a]. When the Si concentration in solution is high, the precipitated layer consists of both hydroxides and hydrosilicates. For glasses with selective leaching as the dominant process, where the precipitation of hydroxide is hindered and the formation of hydrosilicates is favored, the precipitated layer is usually produced with a higher Si content [MENDEL-1984; TROTIGNON-1990b]. Some researchers believe that hydrosilicates, such as calcium hydrosilicates, are less soluble for most elements than hydroxides and, therefore, should form preferentially [BARRET-1986; PETIT-1989].

Lee and Clark [LEE-1985] showed that there is a relationship between zeta potential of the glass surface and colloid formation. In aqueous solutions, the deprotonation process produces $\equiv$Si-O$^-$ groups on the glass and results in an initially high negative surface potential at the glass/solution interface. The ion-exchange reactions also increase the solution pH and decrease the glass zeta potential (Note: The charge at the glass surface is partially balanced by a layer of counter-ions known as the Stern layer. Additional counter-ions are attracted to the surface but are repelled by the Stern layer, causing the development of a diffuse layer of counter-ions. The electrical potential at or near the outer limit of the Stern layer is referenced as the zeta potential). It was suggested [LEE-1985] that as the solution pH increases, metal ions hydrolyze and adsorb onto the glass surface, causing the glass zeta potential to become less negative. Metal cations can also react with monosilicic acid and form charged colloids in the solution. The stability of colloidal particles in the solution depends mainly on the zeta potentials of the glass and the colloidal particles. If oppositely charged or similarly charged but with low potentials, these particles may be adsorbed onto the glass surface. If the colloids have the same sign as the glass and relatively high zeta potential, they are repelled from the glass surface and grow in the solution [LEE-1985].

Amorphous precipitates can act as precursors for subsequent crystalline phase formation. Some of these precipitates incorporate actinides [MENDEL-1984; HENCH-1986a; TROTIGNON-1990b], which in turn influences the release of those radionuclides [MENDEL-1984; HENCH-1986a].

2.1.2.2 Chemical Composition of Surface Layers

The composition of the surface layers depends on leachate chemistry, glass composition, interaction with other materials, such as canister metals, clays, and salts, and test conditions [HENCH-1978, -1986a; MENDEL-1984; BATES-1990a; LUO-1991]. Pickering and Walker [PICKERING-1982] observed an Al-rich layer on a waste glass containing 10 wt.% alumina and a Ca-rich layer on another waste glass containing only 2% alumina. Pickering and Walker explained that when the glass was exposed to leachant, the ion-exchange reaction increased the leachate pH, and Al in the glass was converted to $Al(OH)_3$, which buffered the pH of the leachant at its original value. In glasses where the Al content was insufficient to buffer the pH, $Ca(OH)_2$ was precipitated. In studying surface layer formation during leaching of MCC-DWRG (SRL 165), SRL TDS-131, ICPP-127, and PNL 76-68 glasses in water at 90°C, Houser and Pantano [HOUSER-1985] found that the sequence and composition of the surface layers depended on the sequential attainment of solubility limits in solution, the adsorption or precipitation of insoluble hydrates at the glass/water interface, and subsequent incorporation of these insoluble hydrates behind the advancing reaction front. Surface layer compositions also reflected aging and progressive crystallization. However, Murakami et al. [MURAKAMI-1989] found that the layer compositions for a one-day experiment were not similar to the compositions of the innermost portions of 3- and 14-day layers, as would be expected if changing layer composition reflected only aging and progressive crystallization. Changes in the degree of structural order within the surface layers on SRL 131 glass reacted in deionized water at 90°C for

546 days were reported by Abrajano et al. [ABRAJANO-1990b]. Manara et al. [MANARA-1984a, -1985] reported that the layer composition is a function of redox conditions. They found that more Fe but less U accumulated in the surface layers under oxidizing conditions than under reducing conditions. This was attributed to the fact that Fe^{3+} is less soluble than Fe^{2+}, whereas U^{6+} is more soluble than U in lower valence states.

The chemical stability of the surface layers depends on their composition. Aluminum hydrosilicates are more stable than iron or lanthanum hydrosilicates [TROTIGNON-1990b]. Zinc in the surface layers can make the layers more protective [LEWIS-1982], but the protective effects of the Zn layer can be counteracted by nucleation of Zn-rich clays [TROTIGNON-1990b].

Packing materials can influence the composition of the surface layers [BIBLER-1987; WERME-1990]. Some elements from packing materials can participate in the formation of the surface layers and make the layers more protective [CLARK-1982]. The effects of interactions with other materials on the formation of surface layers has been demonstrated in the results obtained for SRL waste glass buried for up to two years in limestone [NAMBOODRI-1991] and in granite and salt [WILLIAMS-1991].

Common alteration products observed in the testing of HLW glasses have been compiled by Mendel and Bates et al. [MENDEL-1984; BATES-1992b]. Clays and zeolites are the most common alteration products. Iron-rich smectites are abundant if the waste glass contains Fe [BATES-1992b]. Zeolites are common when Al is a constituent of the glass, the flow rate is low, a substantial amount of glass has reacted, and the environment is basic [MORGENSTEIN-1984]. The mineral sequence of alteration products formed in testing R7T7 HLW glass at 300°C has been reported [CAUREL-1990; VERNAZ-1991a] as:

$$[\text{fibrous hydrated zeolites (natrolite)} \rightarrow \text{analcime} \rightarrow \text{Na-feldspar (albite)}]\ .$$

A paragenetic sequence has also been worked out for the alteration assemblage formed by SRL 202U glasses reacted for times of up to 56 days at 200°C in steam as shown in Fig. 2-6 [WRONKIEWICZ-1993]. This sequence indicates that the following temporal paths exist for the major cations leached from the glasses: Na is initially incorporated into herschelite and later into analcime; K is initially incorporated into herschelite, followed by phillipsite, and in later reaction stages is distributed between adularia, illite, weeksite, and mordenite; Ca is incorporated into an unidentified Ca-Si phase; and U is incorporated early into unidentified Na-K-Ca-U-Si web-shaped phases, followed by the formation of a discontinuous U-K-Si surface layer, and finally incorporated into weeksite. Carbonate, sulfate, and phosphate phases have also been observed [BATES-1992b].

2.1.2.3 Physical Behavior of Surface Layers

The physical behavior of surface layers, including cracking during development and exfoliation from the glass surface, may influence the glass reaction rate, colloid formation, and retention of radionuclides [BARKATT-1981b; MENDEL-1984; HENCH-1986a; BATES-1991a; VERNAZ-1991a]. The adherence of surface layers to unreacted glass depends on test duration and conditions, solution composition, layer composition, and crystallinity of the layers. For example, Fig. 2-4 shows that the surface layers formed on SRL 165 glass separate from the glass as the reaction progresses [BATES-1991b]. Crystallization of the amorphous gel layer decreases the adherence of the surface layers to the glass [TROTIGNON-1990b]. The crystallinity of the surface layers may vary according

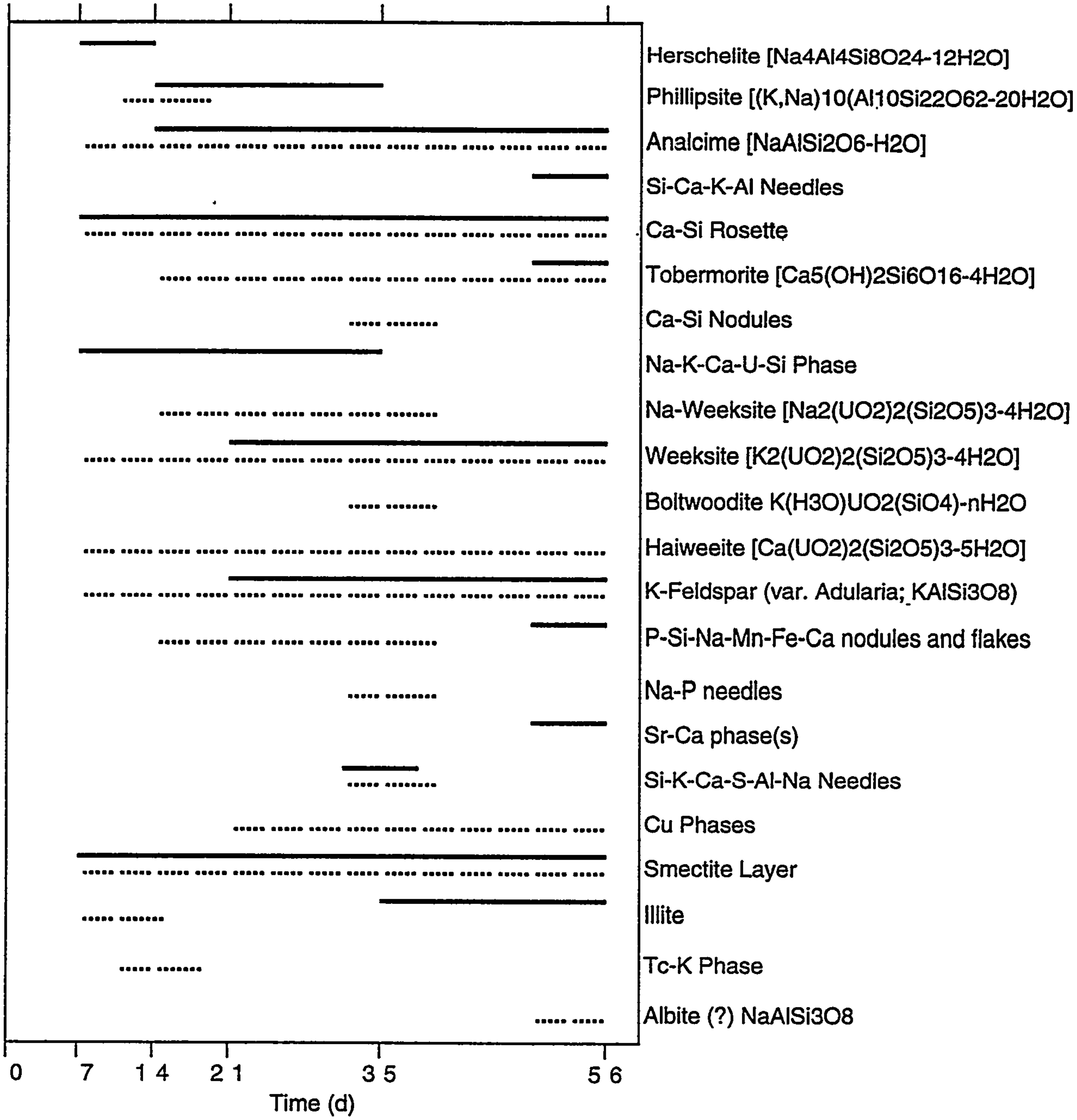


Fig. 2-6. Mineral Paragenesis (adapted from [WRONKIEWICZ-1993]) of SRL 202 Glasses Reacted in a Steam Hydration Test at 200°C. Solid lines represent uranium-doped SRL 202U samples, while dotted lines represent transuranic- and ^{99}Tc-doped SRL 202A samples exposed to an external gamma irradiation field (~3000 rad/h).

to depth of the surface layers [ABRAJANO-1990b] and as a function of test duration [BATES-1991b]. The layer composition may also affect how well the layer adheres to the glass. For example, the presence of Mg and Al causes the surface layers to adhere better to the underlying glass [MALOW-1982; HENCH-1986a; TROTIGNON-1990b]. Increasing the waste loading for SRL 131 glass made the surface layers more adherent to the glass [WICKS-1982a; HENCH-1986a].

Under some conditions, portions of the surface layer can exfoliate (spall) from the glass surface [CLARK-1982; MENDEL-1984; BATES-1991a]. Such spallation of surface layers may constitute a source of colloidal particle formation (see Section 2.7.3). The extent of surface layer cracking depends on the composition (including water content) of the surface layers, the solution composition, and the temperature [CASEY-1990]. Bunker [BUNKER-1983] found a correlation between the appearance of a cracked surface layer and deviation from time$^{1/2}$ dissolution kinetics. The replacement of alkali ions by hydrogen ions during the formation of the surface layers leads to a buildup of stresses because of the change in ionic size and bond energies [BARKATT-1981b; CLARK-1982]. Eventually such a stress may reach a level at which the layer will crack. Hench and Clark [HENCH-1986a] demonstrated that the surface layers showed extensive cracking when leached in pH 1.1 solution where the ion-exchange process was dominant, but the same glass sample leached in higher pH solutions of 10 or 12 exhibited much less cracking. Stress can also be generated if the surface layers undergo crystallization [BARKATT-1981b]. The surface layers have also been shown to adhere better and crack less in silicate water than in deionized water [OVERSBY-1992a]. Surface layers on R7T7 cracked extensively when the test temperature was increased from 90 to 250°C [CAUREL-1990; VERNAZ-1991a]. Barkatt et al. [BARKATT-1991] reported large excursions in leach rate at the end of periods ranging from 1 and 20 months when testing borosilicate waste glasses with a partial-replenishment technique. During these tests, glass leach rates increased by as much as a factor of 20 before dropping back again. This phenomenon was attributed to cracking of the surface layers, where the surface layer was considered to be protective.

2.1.3 Effects of Surface Layers on Glass Corrosion Rate

Surface layers may be "protective" [HENCH-1988; ADAMS-1988; CASEY-1992a]. Protective surface layers can slow the glass corrosion rate by inhibiting mass transport. Nonprotective layers have a porous structure of sparingly soluble solids and adsorbed species that do not significantly inhibit mass transport rates. Several systematic investigations have focused on clarifying the effects of surface layers on glass corrosion [HENCH-1978; CLARK-1981; WICKS-1982b; GRAMBOW-1984a, -1984b; CHICK-1984; CONRADT-1985a, -1985b; VAN ISEGHEM-1990a]. The influence of surface layers on the glass corrosion rate is related to (1) the role of protective layers as physical mass transport barriers that influence the corrosion rates and (2) the role of surface layers in determining glass reaction affinity. The effects of surface layers on radionuclide release are discussed in Section 2.7.2.3.

2.1.3.1 Surface Layers as Mass Transport Barriers

Many discussions in the literature deal with whether or not the surface layers form mass transport (diffusion) barriers that inhibit further glass reactions by inhibiting the transport of reactants and products to or from the reaction zone [HOUSER-1979; BARKATT-1981a; WICKS-1982b; BUCKWALTER-1982a; LEWIS-1982; MALOW-1982; HARVEY-1982; SALES-1982; ISHIGURO-1983; WALLACE-1983; ABRAJANO-1989]. Observed decreases in leach rate with time have also been attributed to the approach to saturation limits of glass components in solutions [GRAMBOW-1983; KUHN-1983; PEDERSON-1983a, -1983b; CROVISIER-1989]. Bourcier

[BOURCIER-1991] has pointed out that it is difficult, if not impossible, to distinguish a glass dissolution mechanism controlled by a diffusion process from another mechanism controlled by the dissolution affinity simply by curve fitting of the solution data. Bourcier has demonstrated that the same data can be explained equally well by either diffusion or dissolution affinity control (see Fig. 3-6 in Volume I). The studies described below were designed to investigate layer effects and to distinguish these from solution saturation effects.

Chick and Pederson [CHICK-1984] performed a systematic investigation to determine whether the glass reaction rate is mainly controlled by diffusion through the surface layers or by solution saturation levels. Four simulated waste glasses with very different compositions were tested using three variations of the MCC-1 test at 90°C for various time periods up to 56 days. The behavior of all the glasses under the various test conditions were found to be the same. In the first variation (set A), samples were reacted for 56 days to generate a surface layer. The same samples were then placed in fresh water and reacted for up to another 56 days. The rate of corrosion decreases with time during the first 56-day leaching period in the standard MCC-1 test (filled squares) as shown in Fig. 2-7a. The rate increases when the leachate is replaced with fresh leachant after 56 days in the variation (set A), but then decreases as the reaction continues (open squares). This shows that surface layers formed during the first 56 days only slightly inhibited corrosion during the second 56 days of reaction. In a second variation of the MCC-1 procedure (set B), samples were reacted for one-half the scheduled reaction time and then removed from the leachate and replaced by a new sample. The new sample was reacted in the same leachate for the remaining time. The results (Fig. 2-7b) indicate that corrosion of a fresh glass sample in a standard MCC-1 test (circles) was almost identical to that of two samples reacted in the same leachate for the same total reaction time (triangles). The results of these tests may be compared to the predictions of saturation-controlled and diffusion-controlled glass corrosion, as shown by the curves in Fig. 2-7. The test results are better modeled by saturation control, although a measurable degree of diffusion control exists.

In a third variation of the MCC-1 test (set C), samples were leached for a scheduled time period in the leachate and then removed, rinsed, and replaced in fresh water at regular intervals of 7, 14, or 28 days. The surface layers grew with each cycle, but saturation effects remained relatively constant. If the glass reaction rate is controlled mainly by diffusion through the surface layers, periodically refreshing the leachant should have negligible effect. If the solution composition controls the reaction, the release curve should be linear because the solution level remains relatively constant. The release curves were nearly linear, with the 7-day replacement tests having the largest slope and the 28-day replacement test the smallest slope, as shown in Fig. 2-8. The normalized release curve in the standard MCC-1 test through 56 days has a slight downward curvature, which indicates that the surface layers provide some barrier to release, but solution saturation is the primary cause of leach-rate retardation.

Conradt et al. [CONRADT-1985a, -1985b] investigated the role of surface layers formed on SM 58 LW 11 HLW glass in a salt brine under hydrothermal conditions at temperatures of 120 and 200°C. The test matrix consisted of five test types with different combinations of manipulations such as layer removal, layer loosening, and leachate replacement with fresh leachants (in layer loosening, the surface layers were separated from the glass sample and broken up; the broken surface layers and the glass samples were then placed back into the leachate to continue the test). Approximately every 42 days, the tests were interrupted for interim manipulations. The total corrosion time was 297 days. The results indicated that the layers were not protective at 200°C. At 120°C, the removal or loosening

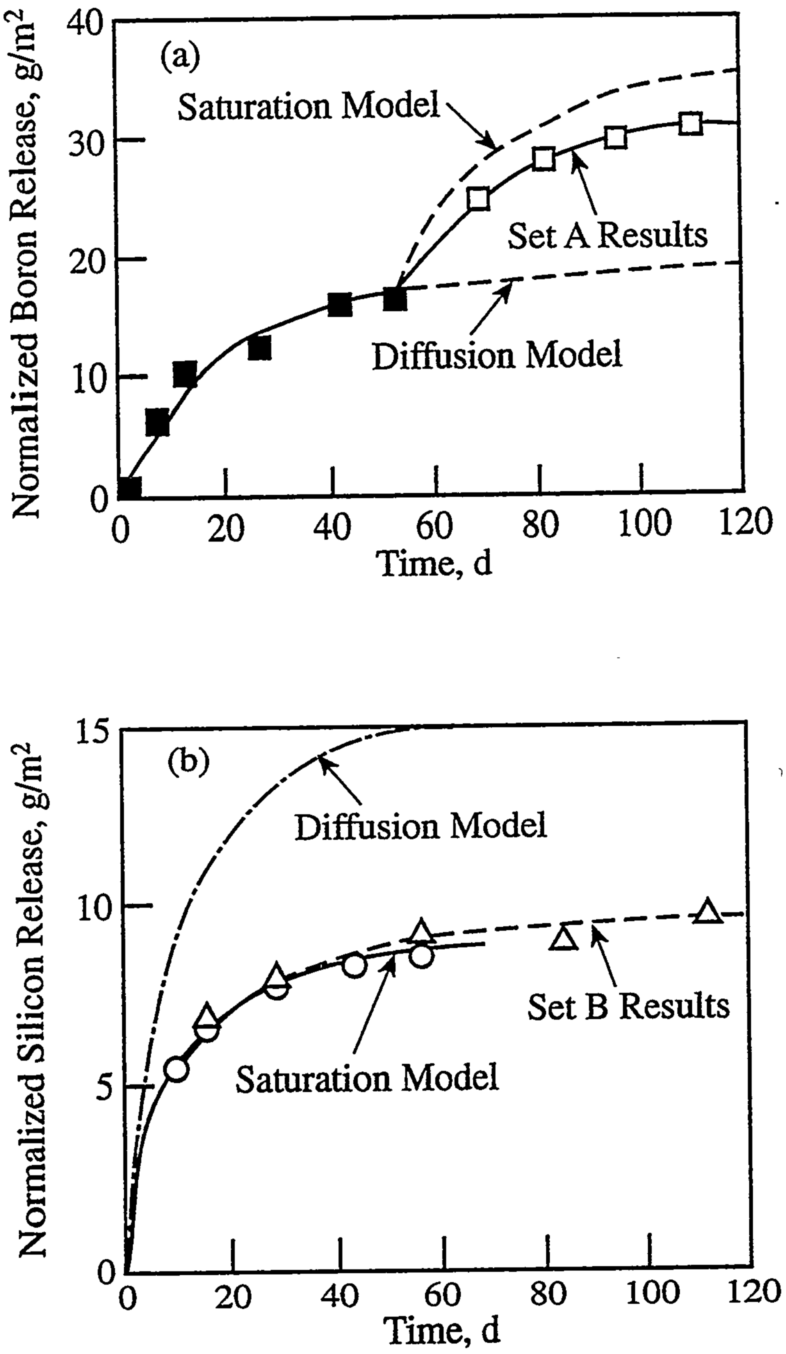


Fig. 2-7. Waste Glasses Tested at 90°C in Deionized Water at 10 m^{-1} (adapted from [CHICK-1984]). (a) Comparison of set A results to solution saturation model and diffusion model. (b) Comparison of set B results to solution saturation model and diffusion model.

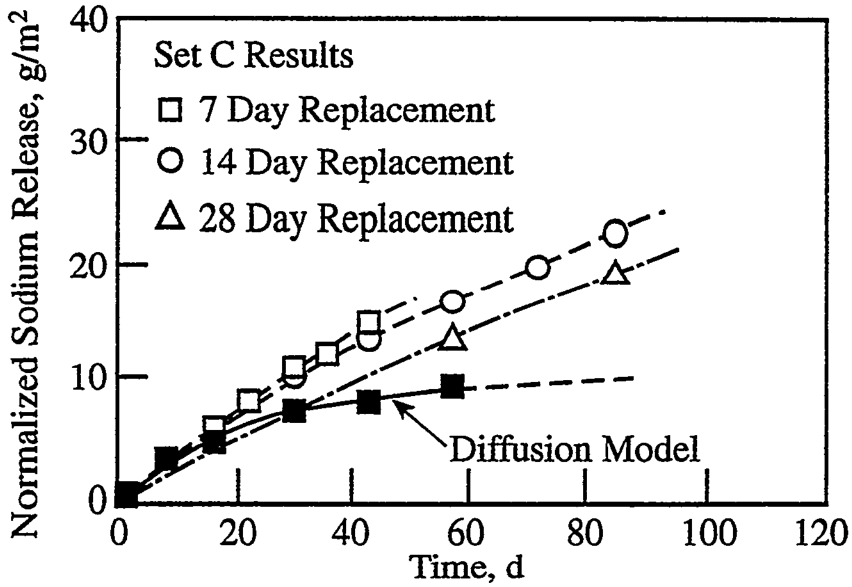


Fig. 2-8. Comparison of Leach between Standard Leaching with Those of Set C at 90°C in Deionized Water (adapted from [CHICK-1984]).

of the surface layers in old brine solution did result in an increased leach rate, although this effect was much smaller than the effects of leachate replenishment, as shown in Fig. 2-9a. This result indicates that the glass reaction is predominately controlled by solution saturation. The slight curvature observed in the normalized weight loss vs. time plots for the leachant replenishment tests (especially at 120°C) may suggest that the layers were providing limited barrier effects. Similar tests on the same glass in 0.01 M NaOH solution (pH = 12.0), as shown in Fig. 2-9b, indicate that the glass reaction rate is almost completely controlled by the surface layers whereas the accumulation of reaction products in the solution has little effect. The reaction rate in the old leachate with the surface layers removed not only substantially exceeded the values of the tests with intact surface layers but also was comparable to those of stripped samples in fresh leachant. This result at pH 12.0 is important because many of the leachates from testing HLW glasses under static conditions have pH values around 12 [FENG-1991a; EBERT-1992].

Van Iseghem et al. [VAN ISEGHEM-1990a] studied the influence of surface layers on the corrosion of SM527, R7T7, and WG124 waste glasses at temperatures between 40 to 190°C for times up to 180 days in a clay-water mixture. Manipulations of the samples included surface layer removal. The results on SM527 and WG124 indicate that the surface layer is somewhat protective only at 190°C. In all other cases, no significant difference was observed between mass loss measured with or without intermediate removal of the surface layers. Surface analysis of the reacted glass samples showed that very extensive layer formation occurred for SM527 and WG124 (between 30 and 100 μm for SM527, and about 120 μm for WG124), but the layer thickness for R7T7 glass was much smaller (≤10 μm). The thicker surface layers are believed to slow glass reaction rates for SM527 and WG124 glasses, and removal of those surface layers slightly increases the glass reaction rate.

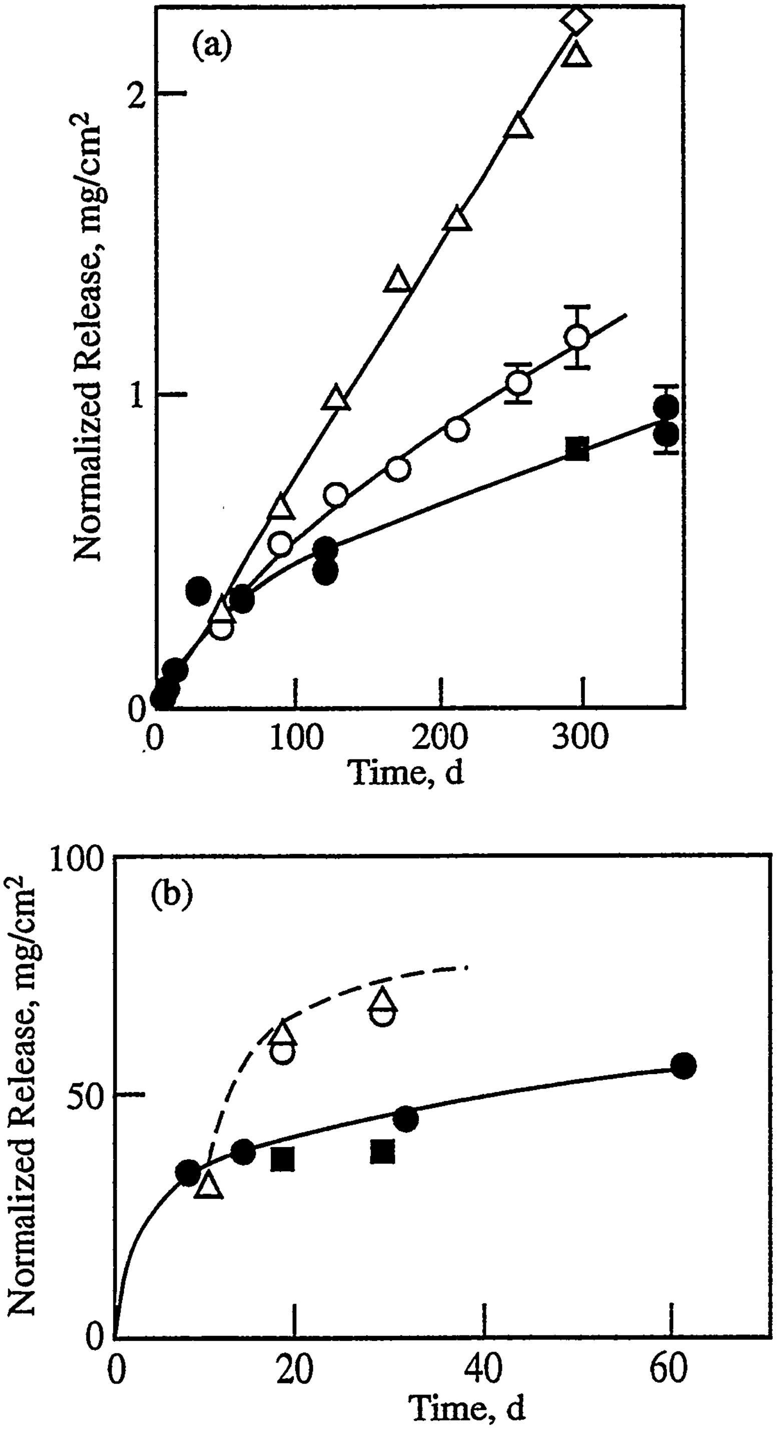


Fig. 2-9. Normalized Weight Loss of SM 58 LW 11 Glass Corroded at 3.4 m^{-1} (adapted from [CONRADT-1985b]) (a) at 120°C in Brine Solution and (b) in 0.01 $\underline{M}$ NaOH solution: (○) = layer loosened samples in old leachate; (◊) = layer covered samples in old leachate; (△) = layer loosened sample in fresh leachant; (■) = no layer or leachant manipulations; and (•) = undisturbed static tests.

Malow [MALOW-1982] observed decreasing leach rates of waste glass C-31 3EC in a solution of $MgCl_2$-$MgSO_4$-NaCl-KCl and found that Mg in the surface layers was enriched by a factor of 10 over the bulk glass composition. The dense and well-adhered surface layers were considered protective and impervious to both leachants and leachates. Hench and Clark [HENCH-1986a] found that the leach rate of SRL 131-29.8% TDS waste glass in 1152 ppm $MgCl_2$ solution was much lower than in deionized water, or in $AlCl_3$ (1028 ppm), $CaCl_2$ (1057 ppm), or $ZnCl_2$ (1025 ppm) solutions under both static and low flow conditions. Examination of the surface layers by SEM showed that the surface layer formed in $MgCl_2$ solution was the least porous and probably served as an efficient transport barrier. Barkatt et al. [BARKATT-1989] found that the leach rates of PNL 76-68, SRL 165, and WV205 waste glasses and microtektites were two orders of magnitude smaller in sea water than in deionized water. Their studies indicated that the formation of an insoluble Mg-rich layer was the major cause for the retardation of glass leaching in sea water. Zhou and Fyfe [ZHOU-1988] observed similar reduction of leach rate for ABS-118 glass in sea water compared to that in deionized water.

Grambow and Strachan [GRAMBOW-1984b] studied the effects of the surface layers formed on PNL 76-68 and C31-3 HLW glasses on corrosion under MCC-1 test conditions in both deionized water and a 0.001 $\underline{M}$ $MgCl_2$ solution. The corrosion of samples with the surface layers removed after 57 days was compared with that of samples without layer removal for reaction times up to 158 days. As shown in Fig. 2-10, the surface layers formed in deionized water (Figs. 2-10a and 2-10b) had no effect on glass reaction, whereas the removal of the layers formed in 0.001 $\underline{M}$ $MgCl_2$ (Figs. 2-10c and 2-10d) showed a factor of three increase in the release rate when the layers were removed. These data are consistent with other studies in Mg-containing solutions [MALOW-1982; HENCH-1986a; BARKATT-1989]. Grambow and Strachan [GRAMBOW-1984b] attributed the rate differences before and after layer removal in $MgCl_2$ solution to the effects of alteration product formation, rather than to the protective effects of the surface layers.

The layers formed on many waste glasses have been interpreted as forming a diffusion barrier for the transport of H_4SiO_4 to the bulk solution [STRACHAN-1983b; MOUCHE-1988; GRAMBOW-1988; -1991]. Strachan [STRACHAN-1983b] proposed that the chemical potential difference between silica in the gel layer and in the unaltered glass can be used as a measure of the driving force for glass dissolution. Grambow [GRAMBOW-1991, -1992b] quantified this diffusion barrier effect. The maximum possible rate of diffusion through the layer is given by the term $(D/L)K^*$ (where D = diffusion coefficient for silica, L = thickness of the transport barrier, and K^* = "saturation concentration" of a silica polymorph) [GRAMBOW-1991, -1992b]. The maximum rate of corrosion is given by the forward rate coefficient, k_f (see Volume I, Section 3.3.2, and Volume II, Section 2.3.1). Silica transport controls the glass reaction rate only if $(D/L)K^*$ is smaller than k_f.

The structure of the surface layers can influence the glass corrosion rate by many orders of magnitude according to a study by Perera and Doremus [PERERA-1991]. They found that some glasses, after hydration, formed an open surface layer [DOREMUS-1983], allowing greater access of water molecules to attack the glass matrix. Glass composition was identified as controlling the surface layer structure. A small amount of alumina in the glass suppressed the formation of a more open structure, thus reducing the rate of corrosion [DOREMUS-1983].

The data of Conradt et al. [CONRADT-1985b] are consistent with those of Chick and Pederson [CHICK-1984]. Both studies found that at a temperature of 120°C or below, the surface layers contributed to the overall glass reaction rate by acting as barriers, although the main control of the reaction rate was through solution saturation. Yangisawa and Sakai [YANGISAWA-1988] also

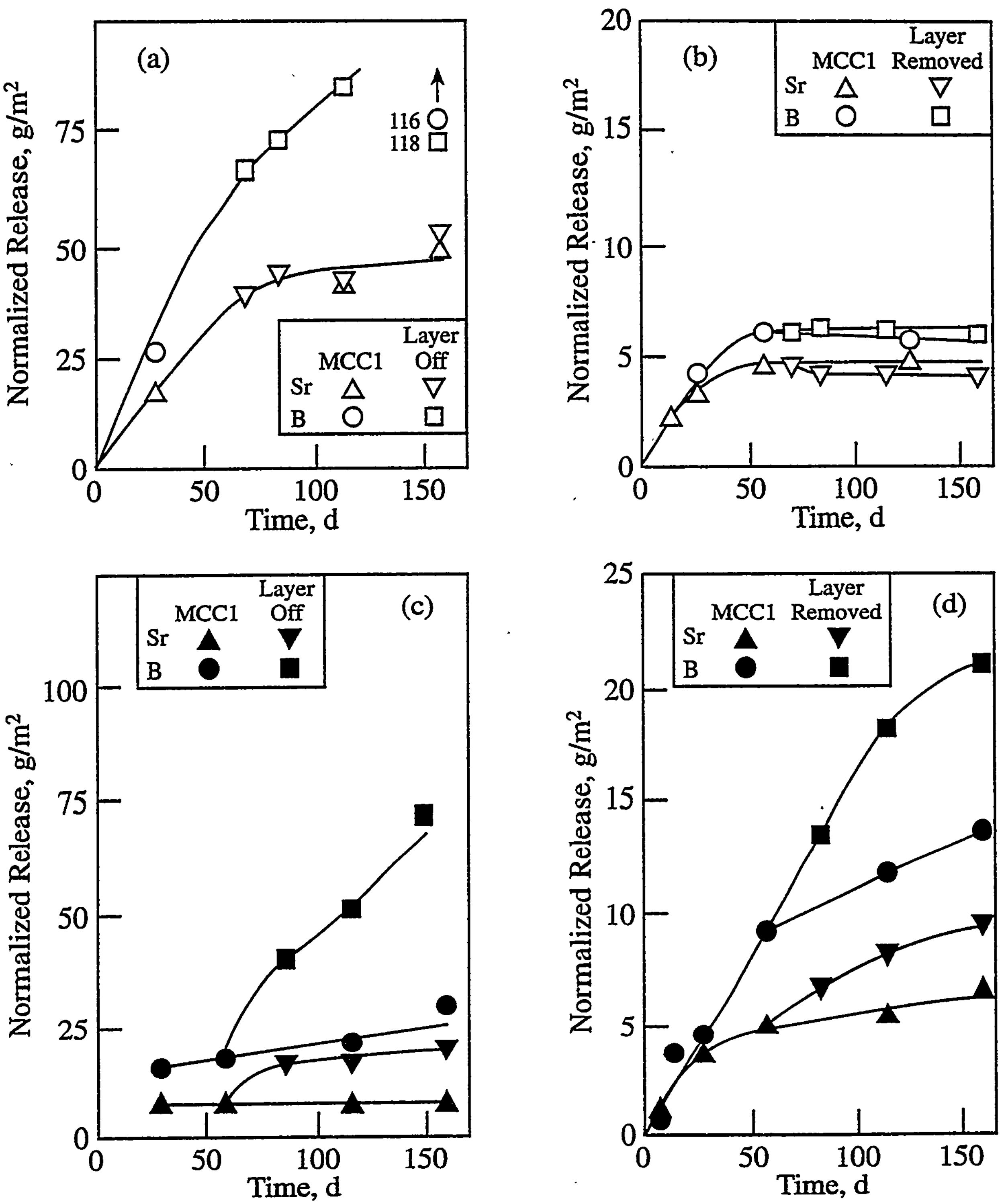


Fig. 2-10. Leach Results under MCC-1 Conditions at 90°C (adapted from [GRAMBOW-1984b]): (a) on PNL 76-68 glass in deionized water; (b) on C31-3 glass in deionized water; (c) on PNL 76-68 glass in 0.001 M $MgCl_2$ solution; and (d) on C31-3 glass in 0.01 M $MgCl_2$ solution.

observed a similar temperature effect on the protectiveness of the layers in the testing of a simulated HLW glass. They found that, for the temperature range of 160 to 210°C, the surface layers that formed on the glass surface could act as diffusion barriers; however, at 240°C, the layers that formed were rather coarse and could not protect glass from further reaction.

In general, the experimental evidence suggests that surface layers can provide a barrier effect to slow down glass reaction, but the extent of this effect depends on glass composition, layer structure and composition, temperature, test conditions, and the silicic acid gradient in the surface layers. The barrier effect is usually much less than the solution composition effect. However, the physical barrier effects of the surface layers on reacted glass may become important in an alkaline solution, in some leachants containing Mg ions, or under conditions in which the matrix dissolution rate is very low. For example, the recent work of Grambow et al. [GRAMBOW-1992a] on testing R7T7 glass in silica-saturated brines showed a square root of time rate dependence in tests up to 800 days. They suggest that the long-term glass corrosion rate may be controlled by water diffusion through the diffusion layer, coupled with glass dissolution processes. Van Iseghem et al. [VAN ISEGHEM-1992] tested borosilicate waste glasses in deionized water at 90 and 150°C, at $S/V = 100$ to $10{,}000\ m^{-1}$, with test durations up to 600 days; the results showed that the long-term dissolution of soluble elements (B, Na, and Li) may be diffusion-controlled. These recent studies suggest that the surface layers may play an important role in long-term glass corrosion.

2.1.3.2 Surface Layer Effects on Glass Dissolution Affinity

Glass dissolution affinity can be expressed as $(1 - Q/K)$, where Q is the activity product of aqueous species involved in the dissolution reaction for the dissolving solid (a gel layer or an amorphous silica phase) and K is the equilibrium constant for that dissolving solid (see Volume I, Section 3.3.2). When a glass reacts with water, the solution concentrations of dissolved glass constituents increase and the solution eventually may become saturated with respect to one or several secondary phases. If secondary phases do not nucleate or if the rate of crystal growth is slow, then the glass reaction is inhibited as the solution concentrations of the components of the dissolving solid increase, i.e., Q increases and glass reaction affinity is reduced. If precipitation of a phase, which lowers the value of Q, occurs at an appreciable rate the reaction affinity will increase. Modeling the glass corrosion rate requires modeling the changes in the affinity term as the reaction proceeds and new phases form.

Surface layers can act as cation sinks which reduce the solution concentrations and increase the affinity for glass dissolution. In hydration experiments on SRL 131, the growth of surface layers initially followed a parabolic rate law; later in the experiment, layers suddenly grew at a much higher rate. Bates et al. [BATES-1982a] suggested a possible connection between accelerated glass reaction and the formation of tobermorite (a hydrated calcium silicate) on the glass surface because this mineral was detected in the precipitated layer after testing times that corresponded with the onset of the accelerated layer growth. It was later suggested that the formation of tobermorite might remove kinetic barriers to outward calcium diffusion and inward water diffusion [ABRAJANO-1989]. Ebert et al. [EBERT-1991a] found that for WVCM44 and WVCM50 waste glasses, reaction rates in steam at 200°C for the first 4 to 5 days were low, but the rates beyond five days were as fast as 2.4 and 21 μm/d, respectively, coincident with the formation of phases such as Li_3PO_4, hydroxyapatite, analcime, weeksite, orthoclase, and a K-containing zeolite. The initial low reaction rates were explained by the saturated solution concentrations in the small volume of the condensed water layer on the glass surfaces, which caused the reaction affinity to approach zero. The reaction acceleration after five days was attributed to reduction of the solution concentration and the consequent increase in the dissolution affinity when crystals nucleated and grew on the reacting surface.

In a comparison test of fully radioactive SRL 200R and simulated 200S at S/V = 20,000 m^{-1} [FENG-1993b], similar corrosion rates were observed initially, but the boron release observed for SRL 200S at 364 days increased by a factor of 40 when mineral phases such as clinoptilolite were formed. No such phases were observed on the surface of SRL 200S before the rate increased. The morphology and composition of the surface layers on SRL 200R were similar to those on SRL 200S before the reaction acceleration. There was no similar reaction increase observed for 200R even after 720 days.

Van Iseghem and Grambow [VAN ISEGHEM-1988a] noted increased glass reaction rates due to formation of analcime when SAN60 glass was tested at 90°C under hydrothermal conditions. Allen et al. [ALLEN-1985] reported accelerated glass reaction coincident with the formation of analcime after reacting SRL 131/TDS-3A glass for 2500 hours at 150°C in the presence of basalt in synthetic basalt groundwater. The rate of increase in Na concentration dropped sharply, probably as a result of analcime precipitation. Strachan et al. [STRACHAN-1985] pointed out that precipitates play an important role in the kinetics of glass reaction through precipitate control of the pH and/or silica concentration.

The assemblage of secondary phases that may form is directly related to the glass composition. Vernaz and Dussossoy [VERNAZ-1992a] concluded from geochemical simulation results that none of the experimentally observed phases (smectite, analcime, albite, or hydrated calcium silicates) is capable of controlling the long-term silicic acid activity, and therefore the long-term reaction rate of R7T7 glass. This conclusion was based on the fact that the Si/Al ratio of R7T7 glass is much higher than those of the aluminosilicates that precipitate, indicating that not enough Al is present to control the Si concentration.

Different assumptions have been made regarding which glass components contribute to the Q and K terms in the glass dissolution affinity expression: (1) amorphous silica phase(s) [GRAMBOW-1985, -1988; STRACHAN-1985; ADVOCAT-1990; VERNAZ-1992a], (2) all components of the glass [JANTZEN-1984a; FENG-1988a; PETIT-1990b], and (3) components retained in the layer [BOURCIER-1990].

Several investigators have suggested that glass dissolution can be modeled using the activity of H_4SiO_4 in solution as the key solution variable [GRAMBOW-1985, -1988; HAAKER-1985; STRACHAN-1985; VERNAZ-1992a]. Grambow and Strachan [GRAMBOW-1988] used amorphous silica phases to approximate the equilibrium constants for JSS-A, PNL 76-68, and SRL 131 waste glasses; different equilibrium constants were used for each glass. The solution data obtained with R7T7 glass reacted at 100°C in water for test times up to one year were also modeled assuming affinity control by amorphous silica [ADVOCAT-1990]. The optimum saturation activity of H_4SiO_4 varies with the glass composition [GRAMBOW-1988] and with the test condition [VERNAZ-1989], although these variations were usually much less than an order of magnitude [GRAMBOW-1988]. The proposed silica phase has never been identified in reacted glass surface layers, although Feng et al. [FENG-1993b] have recently reported finding an almost pure amorphous SiO_2 phase in the surface layers of SRL 200S glass after reacting at S/V = 20,000 m^{-1} for 182 days. With silicic acid control of the reaction, an increase in silicic acid generally causes a decrease in the reaction rate. Hermansson et al. [HERMANSSON-1984] reported more rapid leaching of soluble elements (e.g., B) from some waste glasses in silicate water than in deionized water. A probable explanation for this result is that the pH effect on the reaction dominated the affinity effect because the pH of silicate water was much higher and saturation was not attained in either silicate water or deionized water.

It has been observed that glass corrosion does not cease when silica saturation is reached. Petit et al. [PETIT-1990b] investigated the leach behavior of R7T7 glass at 120°C in a static test system using a combination of glass powders and finely polished monolith samples. Their results indicate that even after silica had reached saturation, the release of soluble components from the glass continued, albeit at a low rate. They suggested that, besides silica, major glass constituents, such as alkali elements, should also be considered with regard to affinity control. Lutze et al. [LUTZE-1988a] observed that corrosion of R7T7 glass in brine solution at 110 to 190°C for periods up to 643 days, as evidenced by the continued increase of B concentration in solution, did not cease after silica saturation. Continued leaching of Na and B from a waste glass reacted in a silica-saturated solution has also been observed [LANZA-1988]. It appears that silica is not the only species that controls the glass dissolution affinity.

A different approach is to include contributions from all the components in the bulk glass in calculating the glass reaction affinity. The K term in (1-Q/K) is calculated according to the hydration energy model [PAUL-1977; JANTZEN-1984a], or according to the structural bond strength model [FENG-1988a, -1990a] using all components of the bulk glass. The Q term is determined from the ion activities of all glass components in the leachates. Advocat et al. [ADVOCAT-1990] simulated the reaction of R7T7 glass using a value of K representative of the bulk glass. They found that saturation did not occur during the simulation, and that test results were better simulated using only silicic acid in the K term. However, the Advocat approach is useful in correlating the short-term chemical durability with glass composition, as shown in glass composition optimization studies [JANTZEN-1984a, -1992b].

Bourcier et al. [BOURCIER-1990] have suggested that dissolution of the gel layer rather than dissolution of the glass better represents the rate of waste glass corrosion. In this model, only the constituents of the gel layer are used to compute the K term. The gel is modeled as a solid solution of component phases with the same composition as that measured experimentally. Dissolution data for SRL and West Valley HLW glass compositions have been modeled using gel layer affinity control [BOURCIER-1990; EBERT-1991a; BATES-1992c]. Precipitation of various aluminosilicates observed in glass tests, such as smectites or zeolites, may keep the solution undersaturated with respect to the gel layer and result in a high long-term dissolution rate [VERNAZ-1992a].

2.1.4 Summary

- Alteration layers are formed on the glass surface due to selective leaching of glass components, different solubilities of glass components, and the precipitation of stable secondary phases.

- Surface layers which form during glass corrosion include a diffusion layer, gel layer, and precipitated layers. The gel layer usually accounts for the majority of the layer volume.

- The structure and composition of the layer and its properties depend on the initial glass composition, solution chemistry, and test conditions.

- Clays are commonly formed during corrosion of high-level waste glasses and replace the gel layer as the reaction progresses. Surface layers may influence glass corrosion by: (1) acting as a physical barrier to the transport of reactants and products, and (2) influencing the solution chemistry. Tests with nuclear waste glasses generally show the layers to have only minor protective effects, although diffusion through the layers may be important in the longer term under silica saturation conditions. The phase assemblage in the surface layers influences the corrosion rate principally through its effects on the leachate concentration of species (e.g., silicic acid) that, in turn, influence the network dissolution affinity.

2.2 Glass Matrix Effects

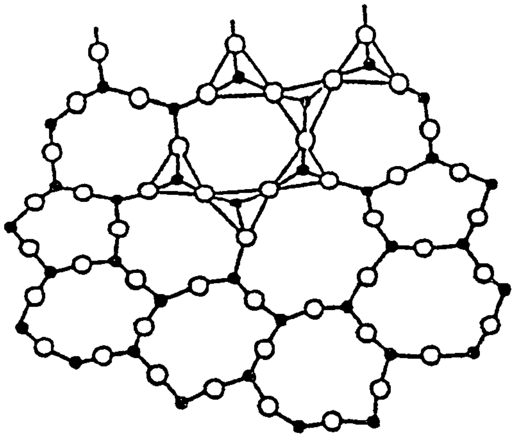
The current understanding of how the structure and composition of the waste glass matrix affect corrosion and radionuclide release is discussed in Sections 2.2.1 through 2.2.5. The discussion includes the effects of (1) bulk glass composition, (2) crystallinity or inhomogeneities within the glass matrix, and (3) reduction/oxidation state (redox) of the glass. A brief review of the current understanding of glass structure is presented in Section 2.2.1.

2.2.1 Glass Structure

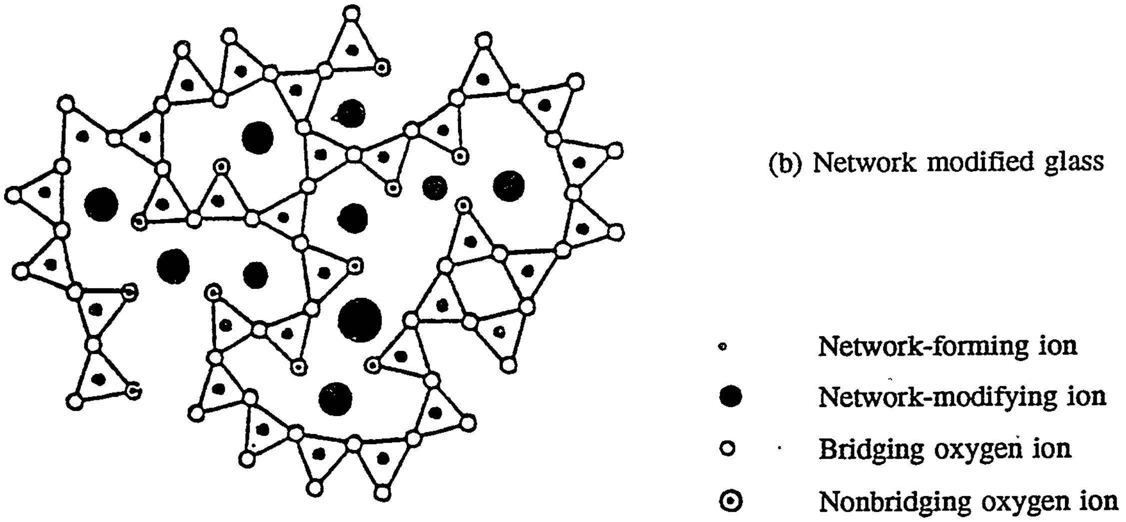
Glass is a term generally used to refer to metastable, inorganic amorphous solids. Glasses have no long-range order (crystallinity). There is disagreement regarding the degree of short-range order. Glass scientists discriminate between a solid (glass) or a liquid (melt) on the basis of a material's internal resistance to flow; solids are materials having a viscosity greater than approximately 10^{15} poise. These concepts have been used to classify a large number of compounds as glasses. The term "glass" is restricted in this document to describing and discussing amorphous inorganic solids, composed primarily of silica (SiO_2). Although several families of glasses have been considered for the isolation of HLW--e.g., borosilicate, aluminosilicate, and Pb-Fe phosphate glasses [LUTZE-1988b; SALES-1985; KAHL-1986]--the focus here is on borosilicate waste glasses.

One of the more widely adopted models of glass structure is the classic random-network model described by Zachariesen [ZACHARIESEN-1932]. In this model, a three-dimensional random network made up primarily of silica tetrahedra (SiO_4) is assumed to form upon cooling of a glass-forming liquid (Fig. 2-11). Each tetrahedron is modeled as being bonded to four other tetrahedra by sharing the apical oxygen atoms, also referred to as bridging oxygen (BO) atoms. In borosilicate waste glasses, Si is considered to be the most important network-forming element. Other elements such as Al can also serve as network-forming atoms by substituting for Si in the Si-O network. Boron, an important constituent of waste glasses, is also thought to serve as a network-forming atom, although the preferential leaching of boron observed in tests is inconsistent with its being a network-former (see Section 1.2 and Volume I, Section 3.2).

Charge compensation is required to maintain charge neutrality when trivalent network-forming components, such as Al^{3+}, B^{3+}, or Fe^{3+}, are included in glass. Alkali or alkaline earth ions serve to balance the charge in the glass network. Alkali and alkaline earth elements can also act as network-modifying atoms when they are incorporated into the glass network at nonbridging oxygen (NBO) atoms. The result is a more open and less connected network. Random network models also include



(a) Pure silica glass



(b) Network modified glass

Fig. 2-11. Conceptual Model of Glass Structure Using the Random Network Model (adapted from [CARMICHAEL-1974]).

a group of elements referred to as intermediates. These intermediate elements are able to serve as both network-forming and network-modifying atoms, depending on the chemistry of the overall glass composition. This class of elements includes Fe, Al, B, and others such as Sb, W, and Mo [STANWORTH-1971].

Despite the wide acceptance of Zachariesen's model, it is not predictive in the sense that it cannot be used to explain or predict many glass properties, including glass durability. Alternative models of glass structure consider some type of agglomeration of microcrystallites [GOODMAN-1985], which are amorphous on a macroscale [WRIGHT-1991; GOODMAN-1985; GASKELL-1991; KOHN-1989]. The dependence of glass corrosion on glass structure is an area that is still being actively investigated [GASKELL-1991; GOODMAN-1985; ELLIOT-1991].

2.2.2 Glass Inhomogeneities

Inhomogeneities may be present in a waste glass due to incomplete melting and homogenization of frit and waste, precipitation of crystallites, phase separation upon cooling of a melt, and devitrification. Any of these processes can cause the final glass to contain separate phases of various sizes and crystallinity. Crystallization has been found in borosilicate waste glasses by many investigators [TURCOTTE-1979; ENGEL-1981; ROBNETT-1981; BICKFORD-1984; MONTROSE-1984; HAAKER-1985; SPILMAN-1986; EDWARDS-1987; STALIOS-1989; BUECHELE-1991; PALMITER-1991; MARRA-1992a, -1992b]. The concern with crystallization is that it may impact the corrosion behavior. Crystallization results in changes in the chemical composition of the glass adjacent to the crystals and causes stresses at the glass/crystal interface. These effects could (individually or in combination) increase glass corrosion. Studies of heat-treated SRL waste glasses have found that spinels, nepheline, and acmite devitrification products occupy 1 to 10% of the total glass volume [BICKFORD-1984; JANTZEN-1983]. Such devitrification was found to have a relatively minor effect on SRL glass leachability in short-term tests [JANTZEN-1985b; HENCH-1982a]. Jantzen et al. [JANTZEN-1985b] found that stresses at the crystal/glass interface increased leaching. For the West Valley Demonstration Project (WVDP) reference glass, water-soluble lithium phosphate crystals have been observed to form in laboratory experiments after extended heat treatment. Such long-term heat treatment is not relevant to the actual processing conditions expected at West Valley [BUECHELE-1991].

For waste glasses that have crystallized, increases in leachability have generally been less than a factor of ten compared to the noncrystallized glass. Spilman et al. [SPILMAN-1986] studied the crystallization of simulated waste glass based on the less durable SRL 131 type glass which was heat treated for periods up to 10 days. They found up to a factor of 40 decrease in MCC-1 leachability for this extensively crystallized (>10 vol.%) glass. Bickford et al. [BICKFORD-1984] and Jantzen et al. [JANTZEN-1985b], studied crystallization of simulated waste glasses based on the more durable SRL 165 type glass. When these glasses were deliberately crystallized up to 30 vol.%, the leachability increased by a factor of three compared to the uncrystallized glass.

The effects of inhomogeneities in West Valley (WV) glasses were investigated [BUECHELE-1991] by considering the effects of composition changes in a single WV glass and the subsequent effects on leachability. Various inhomogeneities were observed, including spinels and acmite. The estimated total volume of the inhomogeneities ranged from approximately 0.1 to 11 vol.%, depending on the heat treatment of the glass.

Simulated Chinese HLW glasses were heat-treated at temperatures between 400 and 900°C by Luo et al. [LUO-1990]. Three different types of crystals--rich in U, Ti, and Ca--formed as a result of the heat treatment. Subsequent leachability testing on this glass indicated that the devitrification had little effect [LUO-1990].

The devitrification for several waste glass compositions, including PNL 76-68, has been studied [TURCOTTE-1979]. Glasses were intentionally devitrified by holding them at 600 to 800°C for up to one year. The extent of crystallinity and the composition of the crystals were strongly dependent on the original glass composition. The effects of devitrification on leaching were addressed in an earlier study [WALD-1979]. Increases in crystallinity (originally 4 to 7 wt.%, devitrified to 9 to 44 wt.%) resulted in increases in leach rates of up to four times the original leach rates. Wald and Westsik

[WALD-1979] ran IAEA leach tests at 25°C for up to 11 weeks and measured the leach rates of Cs, Sr, and Eu. They concluded that the glass composition affected leachability more strongly than did the degree of crystallinity.

2.2.3 Oxidation/Reduction (Redox) State

The oxidation/reduction (redox) state of the glass plays an important role in glass structures which contain polyvalent elements [COLEMAN-1992]. The redox state is determined during glass production and is a function of factors such as added redox-controlling agents (such as formic acid, nitric acid, or sugar) and the glass melt environment. The oxidation state affects important elements such as Fe or Mn by controlling the resultant ionic radii and coordination number within the glass structure. These factors determine whether an element behaves as a network-forming or network-modifying element and how those atoms are released from glass during corrosion. In general, reduced glasses tend to be less durable and less viscous than oxidized glasses. Feng et al. [FENG-1989] reported that the MCC-3 normalized release of Na and B into deionized water for a low-Al glass of poor durability (WV205) increased by a factor of 12 as the (Fe^{2+}/total Fe) ratio was increased from 0.01 to 0.19 (more reduced), as shown in Fig. 2-12. For glass that was initially more durable (WVM50), the leach rate increased by less than a factor of two for a similar change in redox state. The viscosities of these glasses decreased as the redox state increased. This effect has been attributed to the intermediate role Fe can play in the glass network [FENG-1989]. The observation that reduced glasses are less durable is consistent with intermediate elements, such as Fe, becoming network-forming atoms in the glasses under oxidizing conditions. Glasses containing more network-forming atoms are more covalently bonded and less susceptible to corrosion.

2.2.4 Experimental Observations on the Effects of Glass Composition

A wide range of reference glass compositions have been used for testing purposes. The compositions referred to in this section and elsewhere throughout Volumes I and II are presented in Appendix A of Volume I. Experimental studies investigating the effects of glass composition on glass corrosion for simple and HLW glasses are listed in Table 2-1. These studies are discussed in Sections 2.2.4.1 and 2.2.4.2, respectively.

2.2.4.1 Composition Effects in Simple Glasses

Tests performed with simple glasses provide insight regarding the specific effects of different elements which facilitate the understanding of composition effects in chemically more complex glasses. The effect of substituting divalent cations for silica on the corrosion of alkali-alkaline earth-silicate glasses has been the subject of several investigations [SMETS-1984; RANA-1961a, -1961b; ISARD-1986]. Smets investigated glasses in the system $20Na_2O \cdot XRO \cdot (80-X)SiO_2$ (R = Ca, Mg, Zn; X = 0, 5, 10, 15 mol.%). Glass monoliths of various compositions were reacted in hydrothermal leach tests with deionized water between 60 and 90°C for up to 16 hours [SMETS-1984]. Sodium, divalent-cations, and hydrogen profiles in the leached layer were examined using SIMS. The depth of Na depletion was the same as the depth of H enrichment. The SIMS analyses indicated that the release of Na to solution for low (<10 mol.%) divalent-cation glasses decreased nonlinearly as CaO was added. Divalent cations were not significantly depleted from any glasses containing low amounts of divalent cations. Glasses with greater than 15 mol.% divalent cations were found to be appreciably depleted of these species at the glass surface.

Table 2-1. Empirical Studies of the Effect of Glass Composition on Leach Rates

Glass Composition	Variable Elements	Durability Test Type	Durability Test Length	Reference
Simple glasses	SiO_2, CaO, MgO, ZnO	Altered MCC-1	16 (hours)	SMETS-1984
Simple glasses	SiO_2, Na_2O, K_2O, CaO	Altered MCC-1	83 (hours)	RANA-1961a
Simple glasses	MgO, CaO, SrO, BaO	Hydrothermal	700 (hours)	ISARD-1986
Simple glasses	SiO_2, Al_2O_3	Altered MCC-1	16 (hours)	SMETS-1982
Simple glasses	Na_2O, K_2O	Hydrothermal	14 (days)	DILMORE-1978
TRUW, ref. glasses	Al_2O_3, FeO_x	Hydrothermal	243 (days)	VAN ISEGHEM-1984
SAN60, SM58, UK209, SON58, SON64	SiO_2, FeO_x, Al_2O_3, UO_2, Na_2O, Cs_2O, SrO, MgO, CaO, B_2O_3	Hydrothermal	80 (days)	VAN ISEGHEM-1985
M1, M2, M3, M4, M5, M6, M7	SiO_2, Al_2O_3, Na_2O, B_2O_3 FeO_x, CaO, MgO, MoO_3	MCC-1	28 (days)	NOGUES-1982a
ABS39, ABS41	Fe_2O_3, ZnO	MCC-1	28 (days)	NOGUES-1982b
WV205	SiO_2, ZrO_2, FeO_x, ZnO, Al_2O_3, TiO_2, CuO, Cr_2O_3, NiO, La_2O_3	Hydrothermal	56 (days)	FENG-1988a
WV205	SiO_2, ZrO_2, FeO_x, Al_2O_3, Li_2O, B_2O_3, Li_2O, Na_2O, K_2O, MgO, CaO	Hydrothermal	180 (days)	FENG-1989
International waste glasses	SiO_2, ZrO_2, FeO_x, SrO, Al_2O_3, MnO_2, Na_2O, Cs_2O, MgO, CaO, B_2O_3	MCC-1	28 (days)	WICKS-1985
SRL131	Cs_2O, SrO, UO_2	MCC-1	28 (days)	HENCH-1982a
ABS39, ABS41	Fe_2O_3, ZnO	MCC-1	28 (days)	NOGUES-1982b
YN500, YN600	Fe_2O_3, K_2O	Hydrothermal	28 (days)	YANGISAWA-1987
HLW glass	SiO_2, B_2O_3, Al_2O_3, CaO, MgO, Na_2O, ZnO, TiO_2, Cr_2O_3, Fe_2O_3, NiO	Hydrothermal	28 days	CHICK-1981
Simple and simulated HLW glass	SiO_2, B_2O_3, Al_2O_3, CaO, Na_2O	ISO leach test	365 days	TAIT-1983
WV2056, WVCM 507	SiO_2, Al_2O_3, Fe_2O_3. B_2O_3, K_2O, Na_2O, Li_2O	Pulsed flow	100 (days)	BARKATT-1988

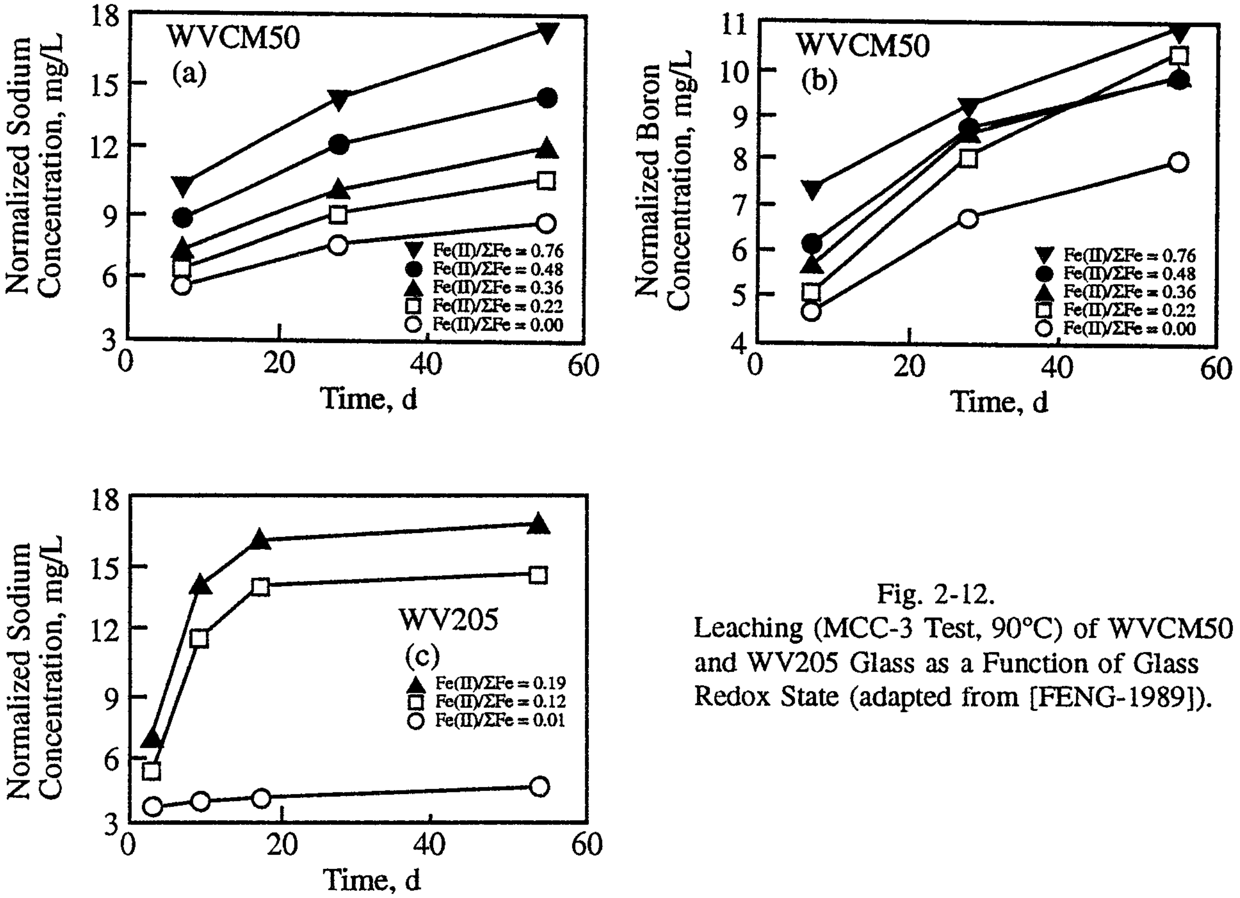


Fig. 2-12.
Leaching (MCC-3 Test, 90°C) of WVCM50 and WV205 Glass as a Function of Glass Redox State (adapted from [FENG-1989]).

The decreased glass leach rates resulting from adding divalent cations to glass were considered to have resulted from a dipole interaction between inwardly diffused H_2O molecules and polarizing divalent cations (e.g., Ca^{2+}) present in the glass. When CaO is added to glass, Ca^{2+} ions are thought to be retained in a leached layer and block the diffusional pathways of H_2O molecules, thereby reducing H_2O mobility in the glass. Initial additions of divalent cations to a glass are believed to be more effective in inhibiting the inward diffusion of water than subsequent additions of divalent cations. Smets et al. [SMETS-1984] reasoned that because of the nature of the reaction, molecular water diffusion, and the inhibitory effect of divalent cations on this process, adding either CaO, MgO, or ZnO to a glass should affect glass leach rates similarly; this conclusion was consistent with their experimental observations.

Eight simple alkali silicate glasses in the system $15(Na_2O,K_2O)\bullet(X)(CaO)\bullet(85\text{-}X)(SiO_2)$, with X = 0, 5, 10, or 15 mol%, were leached in deionized water at 40 to 100°C for up to 83 hours by Rana et al. [RANA-1961a, -1961b]. Reaction progress was monitored by periodically collecting samples of the leachant and measuring the solution concentrations of Na or K, Ca, and Si. Rana's results are consistent with those reported by Smets et al. [SMETS-1984]. Rana also found that sodium silicate glasses are generally more leach resistant than potassium silicate glasses.

Simple glasses in the system $15(Na_2O,K_2O)\cdot 10CaO\cdot 75SiO_2$ were hydrothermally reacted by Dilmore et al. in distilled water for up to 14 days at 100°C, using both monolithic ($S/V = 7.7 \times 10^{-3}\ m^{-1}$) and powdered samples ($S/V = 7.7 \times 10^{-2}$ and $7.7 \times 10^{-3}\ m^{-1}$) [DILMORE-1978]. Reaction progress was monitored by measuring the amount of alkali released to solution; limited post-test solids characterization analyses (SEM and IRRS) were reported. The authors found that K-rich glasses released greater numbers of alkali species to solution than did Na-rich glasses [DILMORE-1978]. Incremental substitutions of each alkali element indicated that the effect on leachability was nonlinear; the most leach-resistant glasses tested contained 12 mol.% Na and 3 mol.% K. More than one alkali ion species in the glass structure was thought to decrease the openness of the glass structure, making the glass more impervious to diffusion processes and, consequently, more leach-resistant. The general finding that potassium silicate glasses are less leach-resistant than sodium silicate glasses agrees with the results of Rana [RANA-1961b].

Aluminosilicate glasses with the composition $Na_2O\cdot 0.4Al_2O_3\cdot XRO\cdot(4-X)SiO_2$ (R = Mg, Ca, Sr, Ba; X = 0.0, 0.4 mol%) were hydrothermally reacted in deionized water and pH 6.2 solutions for up to 700 hours at 90°C [ISARD-1986]. Reaction progress was monitored by measuring the amounts of Na released to solution with time. In pH 6.2 solutions, any additions of alkaline earth atoms to the glass resulted in increased glass leach rates; in deionized water solutions, where the pH had risen to values greater than 10, Mg and Ca decreased the leach rates whereas Sr and Ba increased the rates. It was postulated that as the radius of the alkaline earth ion in each glass increased, the leachability of the glass increased due to successively larger "holes" remaining after ion exchange. The result of these holes was thought to be a net decrease in the protective nature of the alteration layers. Isard's results are in general agreement with those reported by both Smets and Rana.

The effect of Al_2O_3 on the durability of simple glasses in the system $20Na_2O\cdot XAl_2O_3\cdot(80-X)SiO_2$, where X = 0, 5, 10, 15, or 20 mol.%, was investigated [SMETS-1982]. A series of glasses were leached at 70°C. Reaction progress was monitored by measuring Na depth profiles on the reacted glass surfaces, using SIMS. The experimental results indicated that the addition of Al_2O_3 to a sodium silicate glass improved its corrosion resistance. This effect was most pronounced upon the initial addition of small quantities of Al_2O_3, causing the closure of broken Si-O-Si bonds in the $20Na_2O\cdot 80SiO_2$ glass. These broken bonds were thought to constitute "water-conducting" pathways through which molecular water is able to penetrate into the glass network. When these pathways are blocked by the introduction of Al_2O_3 to the glass, water diffusion is impeded.

2.2.4.2 Composition Effects in Nuclear Waste Glasses

A systematic study of the effects of varying the composition of WV205 glass on leaching in MCC-3 tests has been reported by Feng et al. [FENG-1989]. Fifty glass compositions were tested for up to 180 days at 90°C in deionized water. Reaction progress was monitored by measuring the change in pH and the solution concentrations of Al, B, K, Li, Na, and Si. Incremental additions of network-forming elements resulted in nonlinear decreases in leaching, as illustrated in Fig. 2-13. High leach-resistant "plateau regions" were observed in composition space. Feng et al. [FENG-1989] rationalized this observation by postulating that the more leachable glasses were "deficient" in network formers with respect to a complete network.

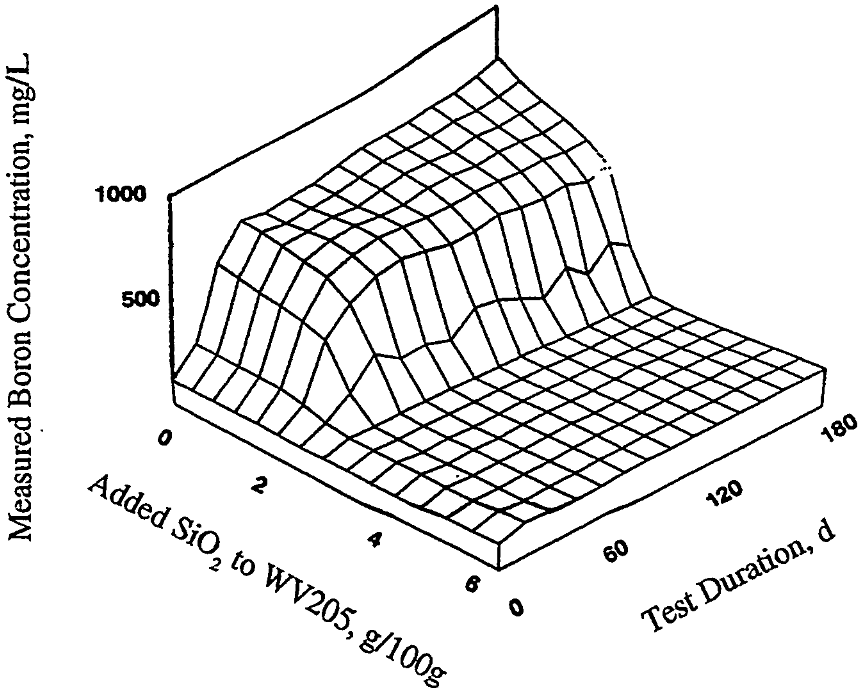


Fig. 2-13. Interpolated Surface Showing the Dependence of MCC-3 Boron Concentration on Test Time and Amount of SiO_2 Added to WV205 Glass (adapted from [FENG-1988b]).

The effects of adding Cs, Sr, and U to SRL 131 glass was evaluated in a series of MCC-1 tests performed at 90°C and $S/V = 10\ m^{-1}$ for 28 days [HENCH-1982a]. The effect of these glass species was investigated by comparing the total mass loss per unit area and the normalized releases of Si, B, Na, Li, Fe, Al, Sr, and Cs. The objective was to evaluate the effect of adding alkali and alkaline earth elements to potential waste glass compositions. The authors observed that glasses containing both Cs and Sr had leach rates approximately 50% lower than that of SRL 131 glass. Furthermore, virtually no Sr and nominal amounts of Cs were released to solution. Additional leaching studies with simple glasses ($15Cs_2O{\bullet}85SiO_2;20Cs_2O{\bullet}80SiO_2;20Cs_2O{\bullet}10SrO{\bullet}70SiO_2$) were performed to further investigate this effect. These tests (performed for 1 hour at 25°C; $S/V = 10\ m^{-1}$) all resulted in similar Si concentrations of about 20 to 25 ppm. The amount of Cs released to solution decreased by a factor of three to four in the Sr-bearing glass. Both SEM micrographs and AES depth profiles of the simple glasses suggested that the alteration layer formed on the Sr-Cs glasses was protective relative to that found on the Cs glasses. Hench and Clark [HENCH-1982a] noted that the decreased leach rates for Cs-Sr glasses appeared to be analogous to that previously found for Na-Ca glasses [e.g., CLARK-1979; SMETS-1984]. While radioactive isotopes of Cs and Sr will have decayed in the long-term timeframe of a geologic repository, these results demonstrate how the presence of network-modifying elements affect waste glass corrosion.

The effect of substituting Al_2O_3 for FeO and Fe_2O_3 in a HLW glass on leach rates was experimentally evaluated for several waste and reference compositions in 90°C hydrothermal leach tests run for up to 243 days [VAN ISEGHEM-1984]. These tests were run to evaluate previous findings that Al_2O_3 could be considered an intermediate with respect to its glass- forming capabilities.

The glasses considered contained 66 to 70 mol.% silica, 0 to 5 mol.% alumina, and 0 to 10 mol.% iron oxide. Two S/V ratios were examined, 100 and 10 m^{-1}. Post-test surface analytical techniques included IRRS, SEM/EDS, and AES with Ar-ion milling. Analyses of the leachate concentrations indicated that the glass dissolved nonstoichiometrically at an S/V ratio of 100 m^{-1} [VAN ISEGHEM-1984]. The Al-containing glass caused the leachate to reach what was described as "saturation" (i.e., the concentrations of species in solution reached constant values) after approximately 10 days, whereas the cation concentrations in the leachate for a similar Al-free glass were still increasing after 80 days. At lower S/V, evidence was found for diffusion and matrix dissolution processes. After one month of reaction, the surface layers formed on the Al-containing glass were about 0.4 μm thick, whereas the layers formed on Al-free glasses (enriched in Fe and Mg) were about 20 μm thick. It was concluded that the substitution of Al for Fe resulted in decreased leach rates by reducing diffusion-controlled leaching (ion exchange) and accelerating saturation of the leachate [VAN ISEGHEM-1984]. The results reported by Van Iseghem et al. [VAN ISEGHEM-1984] support the findings of others that increasing the Al_2O_3 content of a glass decreases its short-term leachability [c.f. SMETS-1982; NOGUES-1982a, -1985]. However, it has been shown that Al can also decrease glass durability [VAN ISEGHEM-1988a] if the dominant reaction process changes. This latter effect has been interpreted to be due to the formation of analcime, which lowers the silicon concentration in solution and thereby increases the reaction affinity. It appears that Al may reduce the initial corrosion rate through its effect on the glass structure but then increase the rate by its effect on the solution chemistry.

The effect of glass composition on the long-term durability of nuclear waste glass is an issue that has been addressed in relatively few experimental studies [LUTZE-1988b, p. 115; VAN ISEGHEM-1992]. The long-term durability effect of Al (from 7 to 18 mol.%) in borosilicate waste glasses designed to resemble waste glass SAN60 has been reported [VAN ISEGHEM-1992]. Durability was measured by monitoring boron, sodium, and lithium release in 90 and 150°C corrosion tests where the S/V ratio was kept constant between 100 and 10,000 m^{-1} for up to 400 days. From the data presented, the authors concluded that diffusion processes, rather than dissolution, are rate-controlling in the long term for all of the glass compositions studied. The authors pointed out that this mechanism results in sharply decreasing corrosion rates with time and that these rates would be considerably lower than those based on determination of a long-term rate from experimental data where dissolution control is the operative mechanism. Aluminum was found to have an important role in short-term corrosion tests due to its effect on the glass network structure [TROTIGNON-1992].

The effect of substituting Fe_2O_3 for ZnO on the leachability, measured using MCC-1 leach tests, of two Swedish borosilicate waste glasses (ABS39 and ABS41) was reported by Nogues et al. [NOGUES-1982b]. Leach tests were conducted with deionized water at 90°C, S/V = 10 and 100 m^{-1} for up to 28 days. In addition to leachate analyses, post-test characterization also included IRRS. The results of this study indicated that adding Fe to these glass compositions increased their leach rates. These results differ from the results reported by Feng et al. [FENG-1989], which indicated that Fe additions decreased leach rates in WV-205 glass. In glasses where half of the Zn content (originally 6 wt.%) was replaced with Fe, the normalized leach rates for Si, B, Fe, Na, and Mo increased by nearly a factor of three, while the normalized release rate for Al was unchanged. The authors concluded that, for this alkali zinc borosilicate glass composition, the leaching at 90°C was enhanced by the substitution of Fe for Zn. Surface analysis suggested that a "critical concentration" of multivalent ions might be necessary for the surface to develop a protective film overlying the SiO_2-rich layer, which results from dealkalization. Apparently, a higher concentration of multivalent elements is needed to stabilize the protective film than would be needed if only one species concentrated in the film. The critical concentration depends on the species present.

The stability of seven simple waste glass compositions were evaluated using MCC-1 test conditions at 90°C for up to 28 days [NOGUES-1982a]. The glasses tested fell within a relatively narrow compositional range that was not systematically varied. The goal of the study was to determine rankings for seven candidate borosilicate waste glasses using several durability measures, including release of elements (Na, B, or Si) to solution as a function of time (deemed the most important durability measure), final pH, and surface analyses by IRRS. The relative amounts of corrosion in the alteration layer were estimated with IRRS by comparing the unreacted glass spectra with the reacted glass spectra and qualitatively assessing the effects of the reaction. Each durability measure had slightly different relative rankings for each glass, which were subsequently used to devise overall rankings. It was concluded that small additions of Al_2O_3 resulted in large decreases in leach rates and, on the basis of the IRRS analyses, that small amounts of Fe_2O_3 were necessary to form an Al-Fe-rich outer alteration layer that reduced further glass corrosion [NOGUES-1982a]. It was also concluded that total (SiO_2 + Al_2O_3) contents greater than 51 wt.% and (SiO_2 + Al_2O_3 + Fe_2O_3) contents greater than 54 wt.% were necessary for what the authors considered to be "good durability." The most leach-resistant glass met these conditions, even though it also had the greatest amount of Na. The observation that additions of alumina to glass results in decreased leach rates is consistent with results found by others [SMETS-1982; NOGUES-1982a; VAN ISEGHEM-1984].

Hench et al. tested 22 glass compositions, including SRL 131 and PNL 76-68, using MCC-1 tests with deionized water for 28 days [HENCH-1982a]. The results were presented in a series of ternary diagrams depicting glass compositions that met specific durability criteria (e.g., 28-day Si release of less than 45 $g/m^2/d$). These plots were used to derive compositional fields, within which it was assumed the minimum leachability was known. Two sets of variables were considered for the ternary diagrams ([Si]:[B + Na]:[Al + Fe + WP]) and ([Si]:[B + Al + Fe]:[Na + WP]), where WP = waste elements. The release of Na and Si was examined and considered to be representative of the release of glass network-modifying and networking-forming atoms, respectively. The results of this study indicated that after 28 days, the release to solution of both glass network-modifying and glass network-forming atoms was the same. A "critical composition" of at least 52 wt.% SiO_2 (to control Si leaching) and 5 to 7 wt.% B_2O_3 (to control Na leaching) was identified [HENCH-1983].

The effect of varying Fe and K content in simulated waste glasses (YN500 and YN600) was studied by Yangisawa and Sakai [YANGISAWA-1987]. Leach tests in granitic groundwater were performed between 50 and 250°C for up to 28 days. Reaction progress was monitored by measuring the change in the amounts of Na, Si, B, and Mg in solution with time and by collecting depth profiles from the reacted glass surfaces using SIMS. The effect of adding 2 wt.% K to a potassium-free glass had an insignificant effect on the measured leach rates. However, increasing the Fe content from 2 to 7 wt.% (Fe_2O_3 total) drastically affected the leach rates; the low-Fe glass, YN600, formed microfissures in the glass that were easily penetrated by water. The resultant alteration layer was a complex, easily spalled phase that had an indistinct boundary with the unaltered glass. The high-Fe glass, YN500, resisted the formation of microfissures and had a distinct, uniform, intact alteration layer. The reasons for these differences were not addressed [YANGISAWA-1987].

Ninety glass compositions from an 11-component alumino-borosilicate system were tested for several properties, including leachability [CHICK-1981]. Leach tests used to monitor reaction progress included 98°C Soxhlet tests, pH 4-buffered tests at 25°C, and 90°C MCC-1 tests in deionized water for 28 days. Two types of leach tests were performed with powdered glasses: (1) Soxhlet tests with distilled water at 98°C for 24 hours and (2) 25°C leach tests in solutions buffered to pH 4 for 19 hours. Reaction progress was monitored by measuring the weight loss of the glass samples. In both types of tests, increasing the amounts of Ca, Na, and B in the glass increased the amount of leaching whereas increasing the amount of Si decreased the amount of leaching. Increasing the amount of Al in glass decreased the amount of leaching in Soxhlet tests but increased the amount of leaching in the pH-buffered tests. This was attributed to the inability of these glasses to form a protective alteration layer in the pH-buffered solutions because Al is more soluble at low pH [CHICK-1981]. The effects observed in this study [CHICK-1981] are consistent with the RNM model of glass structure if B acts as a network-modifying atom in a fashion similar to reports for WV-205 glass [FENG-1989]. However, the effect of adding Ca to these glasses (i.e., an increase in leachability) [CHICK-1981] is contrary to what has been observed for simple glasses [RANA-1961a, -1961b; SMETS-1984; ISARD-1986]. The effects of increasing amounts of Al on leach test results are different with different leach tests.

A series of alkali aluminosilicate glasses containing up to 2% simulated fission products were leached in ISO static leach tests in deionized water between 25 and 100°C for up to 365 days [TAIT-1983]. The goal of the study was to determine the effects of substituting Na for Al and/or Si and CaO; K_2O for Na_2O; and B_2O_3 for Al_2O_3 in aluminosilicate glasses on leachability [TAIT-1983]. All experiments were conducted with S/V ratios of 10 m^{-1}. Glasses with compositions from the systems $[(0.5\text{-}1.5)Na_2O\cdot(0.5\text{-}1.5)Al_2O_3\cdot(4\text{-}6.67)SiO_2]$, $[(1\text{-}X)Na_2O\cdot(X)K_2O\cdot Al_2O_3\cdot 4SiO_2]$ with mole fractions X = 0, 0.1, 0.2, 0.3, 0.4, or 0.5, $[(1\text{-}X)Na_2O\cdot(X)CaO\cdot Al_2O_3\cdot 4SiO_2]$ with mole fractions X = 0, 0.2, 0.4, 0.6, 0.8, or 1.0, and $[Na_2O\cdot(X)B_2O_3\cdot(1\text{-}X)Al_2O_3\cdot 4SiO_2]$ with mole fractions X = 0, 0.1, 0.2, 0.3, 0.4, or 0.5 were tested. Tests were also performed with 2 wt.% simulated fission products added to the sodium borosilicate glasses. Reaction progress was monitored by measuring the release of Si and Na to solution as a function of time. The authors [TAIT-1983] noted that previous studies of aluminosilicate glass leachability found that small additions of Al_2O_3 to silicate glasses reduced the alkali and silicate short-term leaching rates; the Na release was always greater than the Si release. Apparent activation energies of 54 ± 8 kJ/mol for Si and 32 ± 4 kJ/mol for Na were cited as evidence for differences in reaction mechanisms for the release to solution of the two elements. The lower value for Na release to solution was attributed to a diffusion-limited leaching mechanism, whereas Si release was thought to be controlled by etching [TAIT-1983]. The authors concluded that substituting Na for either Al or Si in these $[(0.5\text{-}1.5)Na_2O\cdot(0.5\text{-}1.5)Al_2O_3\cdot(4\text{-}7)SiO_2]$ glasses had a negligible effect on leach rates (which were approximately constant at 7×10^{-7} $g\cdot m^{-2}\cdot s^{-1}$ at 100°C). This was thought to be due to the absence of NBO bonds in glasses with $Na/Al \leq 1$. It is thought that Al preferentially coordinates tetrahedrally, with Na being associated with the Al as a charge-compensating ion. Therefore, NBO bonds are absent in glasses with low Na/Al molar ratios which results in more leach-resistant glasses. The authors also found that replacing K for Na did not significantly affect leach rates [TAIT-1983], in contrast to what others have observed for glasses in the $(Na_2O\cdot K_2O\cdot CaO\cdot SiO_2)$ system [e.g., DILMORE-1978; RANA-1961a, -1961b].

Replacing Na with Ca resulted in increased Ca and Si release rates but the Na release rate was not affected. This effect was thought to result from Ca ions distorting the glass network around Al sites and introducing NBO silicate sites. Replacing Al atoms with B atoms decreased glass leach rates up to a composition of $(Na_2O\cdot 0.8B_2O_3\cdot 0.2Al_2O_3\cdot 4SiO_2)$. Full replacement of Al with B increased leachability as the Na leach rate increased from 4.6×10^{-8} $g\cdot m^{-2}\cdot s^{-1}$ at 100°C to values reported to be an order of magnitude higher [TAIT-1983]. The increased leach rates may be related to the fact that Al is a better network-forming atom than B.

The general results presented in each of the experimental studies are summarized in Table 2-2. These data are difficult to generalize regarding what effect a particular element may have on glass leach rates. For instance, silica is usually recognized as playing an important role in forming a network around which all glass structure is based. However, experimental results presented by

Table 2-2. Examples of Leaching Experimental Results after Varying Glass Composition

Composition Change	Leach Resistance Response	Comment	Reference
(Ca, Mg, Zn) for Si	Increases	Simple glass	SMETS-1984
(Mg, Ca) for Si	Increases	Simple glass	ISARD-1986
Ca for Si	Increases	Simple glass	RANA-1961a; 1961b
(Sr, Ba) for Si	Decreases	Simple glass	ISARD-1986
(Na, K, Li) for Si	Decreases	Simple glass	DOUGLAS-1967
Na for Si	Negligible	Waste glass	TAIT-1983
Al for Si	Increases	Simple glass	SMETS-1982
Ca for (Na, K)	Decreases	Waste glass	TAIT-1983
Na for Al	Negligible	Waste glass	TAIT-1983
Na for K	Variable	Mixed alkali effect	DILMORE-1978
Na for K	Negligible	No mixed alkali effect	TAIT-1983
Al for Fe	Increases	Waste glass	VAN ISEGHEM-1984
Fe^{3+} for Zn	Decreases	Waste glass	NOGUES-1982b
Increase (Si, Al, Zr)	Increases	Waste glass	FENG-1989; MACEDO-1988
Increase Al	Increases	Waste glass	NOGUES-1982a
Increase (Al, Cr, Si)	Increases	Waste glass, MCC-1 tests	CHICK-1981
Increase Al	Decreases	Waste glass, acid leachate	CHICK-1981
Increase B	Decreases	Waste glass	CHICK-1981
Increase B	Increases	Waste glass	FENG-1989
Increase (Na, Li)	Decreases	Waste glass	DIEBOLD-1986
Increase Alkali	Decreases	Waste glass	FENG-1989; MACEDO-1988

Table 2-2 (Contd.)

Composition Change	Leach Resistance Response	Comment	Reference
Increase (Na, Ca)	Decreases	Waste glass, MCC-1 tests	CHICK-1981
Increase (Mg, Ca)	Negligible	Waste glass	FENG-1989
Increase Ti	Variable	Waste glass	MACEDO-1988
Increase Ti	Increases	Waste glass	CHICK-1981
Increase (Cu, Cr, Ni)	Negligible	Waste glass	MACEDO-1988
Increase La	Increases	Waste glass	MACEDO-1988
Increase Zn	Decreases	Waste glass, MCC-1 tests	CHICK-1981
Increase Zn	Decreases	Waste glass	MACEDO-1988
Fe^{3+} for Fe^{2+}	Increases	Waste glass	FENG-1989
Fe^{3+} for Fe^{2+}	Negligible	Waste glass	VAN ISEGHEM-1984

Rana et al. [RANA-1961a] indicate that the leach rates decrease when Si is replaced by Ca. As shown by Van Iseghem et al. [VAN ISEGHEM-1984, -1988a], the effects of specific elements on the glass corrosion may change as the dominant reaction process changes. Changes in the corrosion behavior may occur due to temperature changes, changes in the contacting solution due to interactions with other materials, or as a natural consequence of the corrosion processes, such as changes in the solution pH. Therefore, any conclusions regarding specific compositional effects must consider the test conditions and the dominant corrosion process.

2.2.5 Correlation and Interpretation of Experimental Results

Several models have been proposed for relating the short-term glass corrosion rate to composition; these models are summarized in Table 2-3. The bases for these models range from the thermodynamic approach of the Free Energy of Hydration (FEH) Model to the empirical approach of the Composition Variability Study (CVS). Each of these models relates a parameter, calculated from the glass composition, to the chemical leachability of the glass through the following empirical equation:

$$\frac{\Delta[c]}{\Delta t} = a \cdot X + b \qquad (1)$$

where a and b are the slope and intercept of a linear regression fit to a set of corrosion data, X is the calculated glass composition parameter, and $\Delta[c]/\Delta t$ is an experimentally measured glass corrosion rate (Note: $\Delta[c]/\Delta t$ measures glass corrosion only after a fixed time t and does not address the time dependence of the rate).

Table 2-3. Correlations of the Effect of Glass Composition on Leachability

Model	Reference	Summary
Free Energy of Hydration Model	PLODINEC-1984; JANTZEN-1984a	Correlates short-term leaching with ΔG°_{hyd} for the glass.
Structural Bond Strength Model	FENG-1988b	Correlates short-term leaching with structural bond strength. The heats of formation of the constituent oxides are used to determine an average characteristic bond strength for the glass.
PNL Statistical Model (CVS)	PIEPEL-1990; HRMA-1992	Correlates short-term leaching with composition for a narrow range of glass compositions using statistical means.

2.2.5.1 Free Energy of Hydration (FEH) Model

The FEH model relates the leach rates of glasses to the standard-state free-energy difference between the bulk unreacted glass and the hydrated alteration products (ΔG°_{hyd}). The relation between the calculated free energy of hydration and the experimentally determined corrosion rate was shown to be a first-order equation of the following general form [JANTZEN-1984a; PLODINEC-1984]:

$$\ln LR_i = k_1 \, \Delta G^{\circ}_{hyd} + k_2 \tag{2}$$

where k_1 and k_2 are empirically determined slope and intercept constants, LR_i is the normalized leach rate of species i from the glass, and ΔG°_{hyd} is the standard-state free energy of hydration of the bulk glass.

In the FEH model, the thermodynamic stability of a glass is expressed with the ΔG°_{hyd} term [PLODINEC-1984; JANTZEN-1984a, -1988]. The ΔG°_{hyd} term is calculated by initially assuming that any glass can be considered to be a mechanical mixture of oxides and crystalline binary orthosilicate species [JANTZEN-1984a, -1986]. Each oxide and silicate species is assumed to react with water to form a hydrated species. For a particular glass, the overall free energy of hydration, ΔG°_{hyd}, is then calculated by summing the free energies of hydration for each component oxide or orthosilicate species in the glass so that

$$(\Delta G^{\circ}_{hyd}) = \sum X_i \bullet (\Delta G^{\circ}_{hyd})_i \tag{3}$$

where $(\Delta G^{\circ}_{hyd})_i$ is the free energy change of the hydration reaction of component i, and X_i is the mole fraction of i in the unreacted glass. Tabulated values for $(\Delta G^{\circ}_{hyd})_i$ are presented in Table 2-4 [JANTZEN-1984a]. For this type of reaction, a free energy difference can be calculated by defining the initial (unreacted) and final (reacted) states for the reactants. The free energy differences specified in Table 2-4 are for a glass composition that is a mixture of oxide and silicates species, which means that the glass composition must be stated in terms of oxide and silicate species. The mole fraction, X_i, is used to apportion free-energy contributions according to the molecular abundance of each oxide or silicate component in the glass. Several important glass-forming species, such as Al and Si, may hydrate via several reactions. In these cases, the preferred free energy values were specified [JANTZEN-1984a].

The calculation of ΔG°_{hyd} was later amended for cases where stable hydration (alteration) products were observed to form on a glass during experiments [JANTZEN-1986]. If the hydration reaction for an observed alteration product $(\Delta G^{\circ}_{hyd})_{obs}$ has a more negative free energy of formation than the theoretical $(\Delta G^{\circ}_{hyd})_i$ for element i (Table 2-4) then $(\Delta G^{\circ}_{hyd})_{obs}$ should be substituted in Eq. 3.

An adjustment is made to the ΔG°_{hyd} term to account for the dissociation of silicic and boric acid that occurs in solution at high pH (>9) [JANTZEN-1986]. The hydration free energies for all silica-containing glasses are adjusted for silicic acid dissociation by adding the following adjustment:

Table 2-4. Calculated Free Energies of Hydration for Glass Components[a] [after JANTZEN-1984a]

Component	Hydrated Species	$(\Delta G^{o}_{hyd})_i$ (kcal/mol)
Cs_2SiO_3	Cs^+,H_2SiO_3	-46.820
K_2SiO_3	K^+, H_2SiO_3	-41.735
$BaSiO_3$	Ba^{+2}, H_2SiO_3	-30.570
Na_2SiO_3	Na^+, H_2SiO_3	-28.815
$SrSiO_3$	Sr^{+2}, H_2SiO_3	-24.400
Li_2SiO_3	Li^+, H_2SiO_3	-22.740
$CaSiO_3$	Ca^{+2}, H_2SiO_3	-16.116
$MnSiO_3$	Mn^{+2}, H_2SiO_3	-14.871
$FeSiO_3$	Fe^{+2}, H_2SiO_3	-14.609
$NiSiO_3$	Ni^{+2}, H_2SiO_3	-14.347
$MgSiO_3$	Mg^{+2}, H_2SiO_3	-13.888
B_2O_3	H_3BO_3	-9.930
Al_2O_3	$Al(OH)_3$	-7.73
Al_2O_3	$Al(OH)_2$	-1.63
Al_2O_3	$Al(OH)_3$(am)	+3.04
UO_2	$U(OH)_4$	+8.38
SiO_2	H_2SiO_3[b]	+5.59
Fe_2O_3	$Fe(OH)_3$	+15.50
TiO_2	$TiO(OH)_2$	+15.99
$ZrSiO_4$	$ZrO(OH)^+$, H_2SiO_3	+45.10

[a] $(\Delta G^{o}_{hyd})_i$ calculated from room temperature thermodynamic values. Values of crystalline silicates are substituted when data for amorphous species are not available. The values given assume that silicic acid dissociation at pH values of >9.5 has not occurred. Additional terms representing silicic acid dissociation should be added for leachates that exceed this value.

[b] Value specified by Paul for $\Delta G°SiO_2$ (kcal/mol). Jantzen suggests that more realistic values between +3.7 or +3.76 (kcal/mol) may apply for vitreous silica [JANTZEN-1984a].

$$\Delta\,(\Delta G^{\circ}_{hyd}) = 1.364\ [-\log\,(1 + \frac{10^{-10}}{10^{-pH}} + \frac{10^{-21.994}}{10^{-2pH}}\,)]. \qquad (4)$$

A similar correction is made to correct for the effect of boric acid dissociation reactions at high pH. For these reactions, the following equation is used to calculate a second term added to the ΔG°_{hyd} term to correct for boric acid dissociations:

$$\Delta\,(\Delta G^{\circ}_{hyd}) = 1.364\ [-\log\,(1 + \frac{10^{-9.18}}{10^{-pH}} + \frac{10^{-21.89}}{10^{-2pH}} + \frac{10^{-35.69}}{10^{-3pH}}\,)]. \qquad (5)$$

Both corrections (Eqs. 4 and 5) are applied for glasses containing both Si and B. The equations were derived from the known dissociation constants of silicic and boric acid at high pH conditions [JANTZEN-1986]. Careful, reproducible measurements of pH are needed because Eqs. 4 and 5 are very pH sensitive. Originally, the correction was proposed for either the ΔG°_{hyd} term or the LR_i term [PLODINEC-1984]. Later descriptions of the FEH model apply the pH correction to the ΔG°_{hyd} term only [JANTZEN-1984b, -1986, -1992b].

2.2.5.2 Structural Bond Strength Model

The Structural Bond Strength (SBS) model is based on structural thermodynamic considerations and has been proposed to describe the chemical leachability and viscosity of HLW glasses [FENG-1988a, -1988b, -1988c, -1989]. The predominant controlling factor is assumed to be the binding strength of the bonds between atoms in the glass. It was thought that the glass-forming tendency of an element is directly proportional to the strength of its oxygen-metal bond, where network formers have bond strengths above 80 kcal/mol [FENG-1989]. The structural bond strengths are obtained from the known heat of formation of the constituent oxides and are subsequently modified by four empirical rules that characterize the different structural roles of particular oxide groups. Based on the RNM model of glass structure, elements are divided into basic groups of network formers (SiO_2, Al_2O_3, and ZrO_2), network modifiers (alkali elements), and intermediates (e.g., TiO_2). Although B_2O_3 is considered to be an excellent glass former, its addition to a silica melt increases the leachability of the resulting glass. In the SBS model, therefore, it is treated as an intermediate glass former.

Four rules were formulated that detail how an element's structural bond strength contributes to the overall average structural bond strength of a glass [FENG-1989]. The average structural bond strength is then calculated by summing the effect of each element according to these rules, such that

$$V = \sum X_i \cdot V_i \qquad (6)$$

where the average structural bond strength of a glass is calculated from the mole fraction, X_i, of each element i multiplied by its structural bond strength contribution, V_i.

The average structural bond strength, V, is related to the chemical leachability of a glass as measured in short-term tests. The concentration of species i in the leachate $[C_i]$ is empirically correlated with V through a form of Eq. 1:

$$\log [C_i] = b \bullet V + a \tag{7}$$

where a and b are the intercept and slope of a linear regression fit to a data set of values of V and leach test results.

2.2.5.3 Other Models

Other correlations between glass composition and glass corrosion have been developed. The nonbridging oxygen (NBO) model assumes that the average number of NBO atoms in an unreacted glass reflects its leachability [JANTZEN-1984a; GELDART-1988]. Glasses with small numbers of ionically bonded NBO atoms will not leach quickly. The valence-oxygen (VO) correlation is based on the assumption that the leachability of a glass is governed by its average valence [GELDART-1988]. This correlation assumes that monovalent cations are bonded most weakly to the glass network. Thus, glasses with a large average valence in the unreacted glass will not leach quickly.

An experimentally based statistical approach, Compositional Variability Study (CVS), was designed at Pacific Northwest Laboratory (PNL) [PIEPEL-1990] to correlate leach-resistance with HLW glass compositions. The overall goal of the CVS is to identify the target glass compositions for HLW vitrification at Hanford. The approach used in the initial empirical study (CVS-I) was to synthesize a number of glasses from the nine major oxide components expected to be in the final waste form. Glasses encompassing the range of compositions expected to be produced at the HWVP were tested for durability with MCC-1 and PCT tests [HRMA-1992]. Tests were performed with deionized water at 90°C for 7 days (PCT: $S/V = 2000\ m^{-1}$) and 28 days (MCC-1: $S/V = 10\ m^{-1}$). Changes in solution concentration of B, Si, Na, Li, and Cs were monitored, although normalized B release was used. This selection was based on the observation that other elements tend to be incorporated into secondary phases that form during glass reactions with water.

The data from each test were fitted to an empirical mixture model of the form

$$r = \exp\left(\sum_{i=1}^{n} a_i\, g_i \right) \tag{8}$$

where r is the normalized B release, g_i is the mass fraction of the i-th component in glass, a_i is the coefficient of the i-th component, and n(=10) is the number of components (SiO_2, B_2O_3, Na_2O, Li_2O, CaO, MgO, Fe_2O_3, Al_2O_3, ZrO_2, and "Others" [composed of other elements which comprise up to 10 wt.% of the glass]) [HRMA-1992]. Linear regression using the first-order CVS model did not fit the data well. The results of CVS-I defined the compositional region of interest that will be studied in detail in CVS-II [PIEPEL-1990].

The empirical correlation of tens of glass compositions and their corresponding normalized silica release values from 28-day MCC-1 tests in deionized water has been presented by Abrajano [ABRAJANO-1988b]. The glass compositions examined included natural, simple, and HLW glasses. The suite of data was examined with the FEH, SBS, NBO, and VO correlations, Fig. 2-14a-d, and fit with a linear regression equation such as Eq. 3. The resultant correlation coefficients were 0.75, 0.62, 0.68, and 0.46 for the FEH, SBS, VO, and NBO correlations, respectively. When the same data were subjected to multiple linear regression analysis (independent of glass composition), the correlation coefficient was 0.80 (Fig. 2-14e).

2.2.6 Summary

- Glass matrix effects on corrosion include those resulting from the glass composition, from the oxidation state of glass components, and from inhomogeneities in the glass. Durability is test sensitive and it is important to understand that durability results can vary with different test methods.

- The effect of glass composition on waste glass durability is difficult to generalize since it is necessary to consider the overall glass composition. As demonstrated in experimental studies, increasing the amount of an element that results in a decreased corrosion rate in one glass composition can have the opposite effect in another glass composition. It has been shown for some waste glass compositions that large increases in glass durability can be achieved with relatively minor changes in glass composition.

- In general, decreasing the amounts of network modifying elements or increasing the amounts of network forming elements in waste glass compositions will enhance the short-term glass durability. For specific glass compositions, the precise effect of each element on glass leachability cannot be definitely described since the glass composition and solution chemistry both affect the glass durability.

- As illustrated by the effects of Al, the short-term effects may be very different from the longer-term effects.

- Glasses with components in high oxidation states tend to be more durable since they act as network forming elements.

- Inhomogeneities in glass matrices have the potential to affect glass corrosion by providing channels for the ingress of water, although studies have shown that this is generally not significant in waste glasses.

- A variety of models have been used to develop linear correlations between short-term durability and waste glass composition.

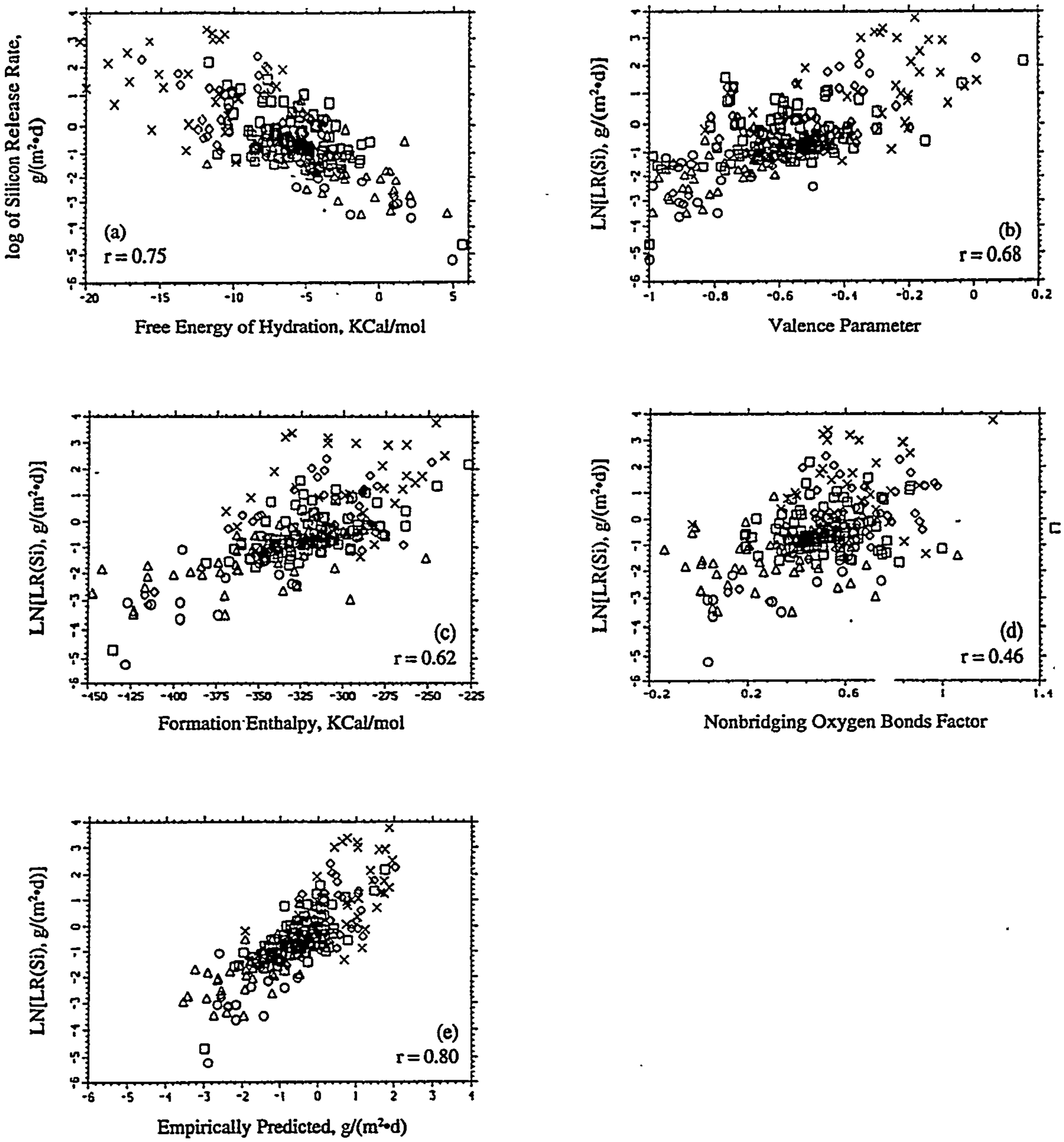


Fig. 2-14. Correlation (r = Correlation Coefficient) of the Log of the Release Rate of Silicon (Ln LR_{Si}) with (a) ΔG^{o}_{hyd}, (b) Valence Parameters, (c) SBS Parameters, (d) NBO Concentration, and (e) Empirically Predicted LR_{Si} for MCC-1, 28-Day Test Results. The symbols indicate the final pH ranges: (X) > 11; (◇) 10-11; (◇) 9-10; (△) 8-9; (○) <8 [modified from [ABRAJANO-1988a]).

2.3 Effects of Solution Composition, Surface Area-to-Solution Volume, and Flow Rate

The composition and chemistry of the fluid which contacts a high-level waste glass will affect the glass corrosion rate and the release of glass components into solution. The fluid chemistry will be determined initially by its interactions with various phases in the host rock, with engineering components such as metal containers and backfill materials, and by radiolysis of the gas phase and the groundwater itself (see Section 3.5). The amounts of dissolved air, iron, and other redox sensitive species are likely to establish the redox potential of the fluid which initially contacts the waste glass (see Volume I, Section 2.2.3.4). The chemistry of the solution in contact with the glass will change as the glass corrodes and glass components are released into solution. These changes will affect both the corrosion rate and the disposition of various glass components as the glass reacts.

The solution composition is known to strongly influence the glass corrosion rate, as discussed in Volume I, Section 3.2, and in Volume II, Section 2.1.3. The silicon content of leachate solutions is generally found to strongly affect the reaction rate under neutral and basic solutions [GRAMBOW-1985], while the aluminum content affects the reaction rate in acidic solutions [BOURCIER-1992]. As will be discussed in detail in Section 2.3.1, the leachate pH also strongly affects the corrosion rate of alkali borosilicate glasses [KNAUSS-1990; ADVOCAT-1991]. In general, the silicon concentration and the leachate pH both increase as the glass corrodes (the pH may decrease in brine solutions due to secondary phase formation); increased silicon concentrations cause the glass corrosion rate to decrease, while the rate increases with higher pH values. The aluminum concentration has little effect on the corrosion rate under basic conditions [BOURCIER-1992]. Other interactions between the leaching solution and its environment which affect the silicon concentration or the pH will also affect the glass corrosion rate, such as the effects of dissolved CO_2 or radiolytically generated acids on the pH and the sorption of silicon by clays and other mineral phases. Other components of natural groundwaters may also affect the corrosion of HLW glasses. For example, qualitative observations of the etching of borosilicate glass by solutions containing humic acids have been reported, although the significance of these observations is not clear because quantitative information was not provided [SCIENCE NEWS-1992].

The Eh and pH of the solution affect the speciation and solubility of some released glass components. The combined effects of the pH and Eh on the durabilities of HLW glasses (in terms of the release of boron and silicon in MCC-1 tests) have been summarized using Pourbaix diagrams [JANTZEN-1992b]. While the solution Eh has little influence on the behavior of glass components having only a single oxidation state, including the alkali metals, boron, and silicon, HLW glasses are slightly less reactive in reducing groundwaters than in oxidizing groundwaters [JANTZEN-1985c].

The Eh and pH of the fluid will also affect the disposition of radioelements between potentially mobile and immobile fractions as the glass corrodes. Actinide elements (designated by An) and technetium have variable oxidation states which may range from An(III) to An(VI) and Tc(II) to Tc(VII), and their speciation and solubilities are very sensitive to their oxidation states. Glass corrosion is expected to significantly alter the chemistry of the contacting fluid from that of the initial groundwater. Therefore, generalizations based on known groundwater chemistries cannot be made, and the unique solution conditions generated during a laboratory test or those predicted by geochemical codes must be addressed individually.

This section considers in detail the effects of the solution composition (primarily the silicic acid concentration and the pH) on the corrosion of the glass matrix, while the disposition of radioelements as the glass corrodes is discussed in Section 2.7. The extent to which corrosion of the glass waste form or other interactions alter the composition of the contacting fluid depends on the amount of groundwater in contact with the glass. Under the conditions expected for HLW repositories, where the volume of groundwater is very low relative to the amount of glass, corrosion of the glass and other interactions are expected to significantly alter the solution chemistry from that of the initial groundwater (see also Section 2.7). Laboratory tests and computer models must properly account for changes in the fluid chemistry due to glass corrosion and its corresponding effects on the glass corrosion.

Two testing parameters that affect the fluid composition at the glass surface are the glass surface area-to-solution volume (S/V) ratio in static tests and the flow rate in dynamic tests. The S/V does not itself affect the glass reaction and is not a reaction parameter as such; rather, it is a test parameter that affects the solution composition. In this ratio, the surface area represents the amount of glass available to react and the solution volume represents the volume available to dilute the reaction products. The results of static leach tests used to monitor production consistency, measure chemical durability, or characterize the reaction mechanism and kinetics are known to be affected by the S/V used in the test [MENDEL-1984, pp. 1.11-1.12]. The dominant physical effect of the S/V is through dilution of the reaction products released into solution;[2] compared with tests at low S/V, tests at high S/V will have less solution available per unit surface area to dilute reaction products and so the leachate solution will become concentrated at a higher rate. Likewise, dynamic leach tests will also be affected by the extent of dilution (or rate of removal) of reaction products that occurs due to replenishment of the leachant by solution flow. Because the glass reaction rate is known to be strongly influenced by solution chemistry (see Section 2.1.3 and Volume I, Section 3.2), the S/V ratio and flow rate must be accounted for when evaluating or comparing the results of different leach tests. The effects of solution chemistry on the glass reaction in static leach tests at different S/V ratios and in dynamic leach tests at different flow rates are discussed in Sections 2.3.1 and 2.3.2, respectively.

2.3.1 S/V Effects in Static Leach Tests

Static leach tests are performed by sealing a specimen (monoliths or powder) of known surface area with a known volume of leachant in a reaction vessel and maintaining the vessel at a constant temperature for a predetermined length of time. At the end of the prescribed duration, the solution is removed and analyzed for dissolved glass components. A primary distinction of different leach tests is the S/V specified by the test. The S/V used in a static leach test was recognized by Hench et al. [HENCH-1977, -1980; ETHRIDGE-1979] to affect the leachate pH in tests with simple silicate glasses. The effects of pH on silicate glass dissolution had been described earlier [DOUGLAS-1967; EL-SHAMY-1972a, -1972b]; in these studies, the extent of Si extraction was very small below about pH 9 but increased rapidly at higher pH values. An increase in pH in tests with alkali-containing glasses is a consequence of the glass reaction (see Section 1.0). The pH dependencies of the ion-exchange and hydrolysis reactions causes one or the other reaction to dominate the glass corrosion process at different solution pH values; ion exchange is promoted at low pH values and hydrolysis is promoted at high pH values. Ethridge et al. [ETHRIDGE-1979] showed that the time required to reach pH values near 9 and change to a hydrolysis-dominated system was correlated with the S/V of the test. The dependence of pH on the test S/V can be explained, at least in part, by simple dilution of the hydroxide generated during the ion-exchange reaction.

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[2] This includes dilution of reaction products from radiolysis reactions and the corrosion of other materials present in the system as well as those from corrosion of the glass itself.

Although the reaction of multicomponent HLW glasses is more complicated than that of simple glasses [McVAY-1980b], similar effects are observed in tests with HLW glasses at different S/V ratios [BUCKWALTER-1982b; ADVOCAT-1991]. In addition to pH, the S/V also affects the concentrations of released glass components. This is important because the solution concentrations of glass components, particularly the Si concentration, may provide dominant control of the corrosion reaction rate of HLW glasses [GRAMBOW-1984a, -1984b, -1991; ADVOCAT-1991], although other species in solution may also affect the reaction [PETIT-1990b; BOURCIER-1992]. Silicic acid has a major influence on the reaction because the glass corrosion process requires the destruction of the silicate network, and silicic acid (or partially dissociated silicic acid) is the solution species that controls the rate of this reaction.

In the Grambow model of the reaction rate (see Volume I, Section 3..3.2.2), the rate equation is derived by assuming that the rate-determining step is molecular water hydrolysis of a terminal $\equiv$Si-O-Si(OH)$_3$ bond to release H_4SiO_4 to solution [GRAMBOW-1984a, -1985, -1987]. The rate of matrix dissolution may be expressed in terms of the loss of H_4SiO_4 groups from the surface as

$$\frac{-dn(H_4SiO_4)}{dt} = S\,k_+\left(1 - \frac{[H_4SiO_4]}{[H_4SiO_4]_{sat}}\right) \tag{9}$$

where n(H_4SiO_4) is the number of moles of H_4SiO_4 released from the glass, S is the glass surface area, k_+ is a forward rate coefficient (which may depend on the pH), [H_4SiO_4] is the solution concentration of silicic acid, and $[H_4SiO_4]_{sat}$ is the "saturation" concentration of silicic acid. A mass transport term is sometimes included in the rate expression as well (see Volume I, Section 3.3.2). If all silicic acid released from the glass remains in solution, that is, if no Si-containing secondary phases form, then the rate may be expressed in terms of the silicic acid solution concentration by substituting [H_4SiO_4] = n(H_4SiO_4)/V, where V is the solution volume. Integration of the rate expression then yields [GRAMBOW-1985]

$$\frac{[H_4SiO_4]}{[H_4SiO_4]_{sat}} = 1 - \exp\left(-\frac{S}{V}\,k_+\,\frac{t}{[H_4SiO_4]_{sat}}\right) \tag{10}$$

Equation 10 shows that the silicic acid concentration [H_4SiO_4] will approach a limiting value of $[H_4SiO_4]_{sat}$ exponentially. The rate at which saturation is approached depends only on the product (S/V)•t, where t is the total reaction time, and not on S or V individually [MACHIELS-1983]. Such a relation between the silicic acid concentration in solution and the product of S/V and the reaction time was proposed by Pederson et al. [PEDERSON-1983b, -1983c] on the basis of observations by Ethridge et al. [ETHRIDGE-1979] and experimental evidence with a simulated HLW glass. This suggests that correlation of experimental data using the (S/V) variable may be a useful approach for characterizing the long-term corrosion of waste glass because it predicts the existence of a unique reaction curve that describes the reaction as a function of (S/V)•t [PEDERSON-1983a, -1983b]. A single curve describing the reaction progress can be constructed from the results of static tests performed at very high S/V over short reaction times (on the order of several months). This curve can then be interpreted as describing the glass reaction at a much lower S/V over extremely long reaction times (on the order of thousands of years) if the reaction mechanism can be assumed to remain the same [PEDERSON-1983a; MENDEL-1984, pg. 1.12; SPINOZA-1986].

Experiments show that solution concentrations correlate with (S/V)•t in some tests but not in others. For example, Fig. 2-15 shows a plot of the B and Si data of Pederson et al. [PEDERSON-1983b] where monolithic samples of PNL 76-68 glass were reacted at S/V values of 1, 10, and 100 m^{-1} in deionized water to generate data corresponding to between about 0.03 and 2800 d/m. A single curve can be drawn through the data for both components from tests at all S/V ratios.

Tests at high S/V are more commonly performed using powdered glass samples, which provide very large surface areas. The surface reactivities of powdered glass and glass monoliths may be different. Powdered glasses have fractured surfaces with smooth facets and sharp edges and corners that may have different reactivities. Monoliths may be ground to varying surface finishes with abrasives or diamond pastes, or they may be fractured. Monoliths may also be reacted with as-cast

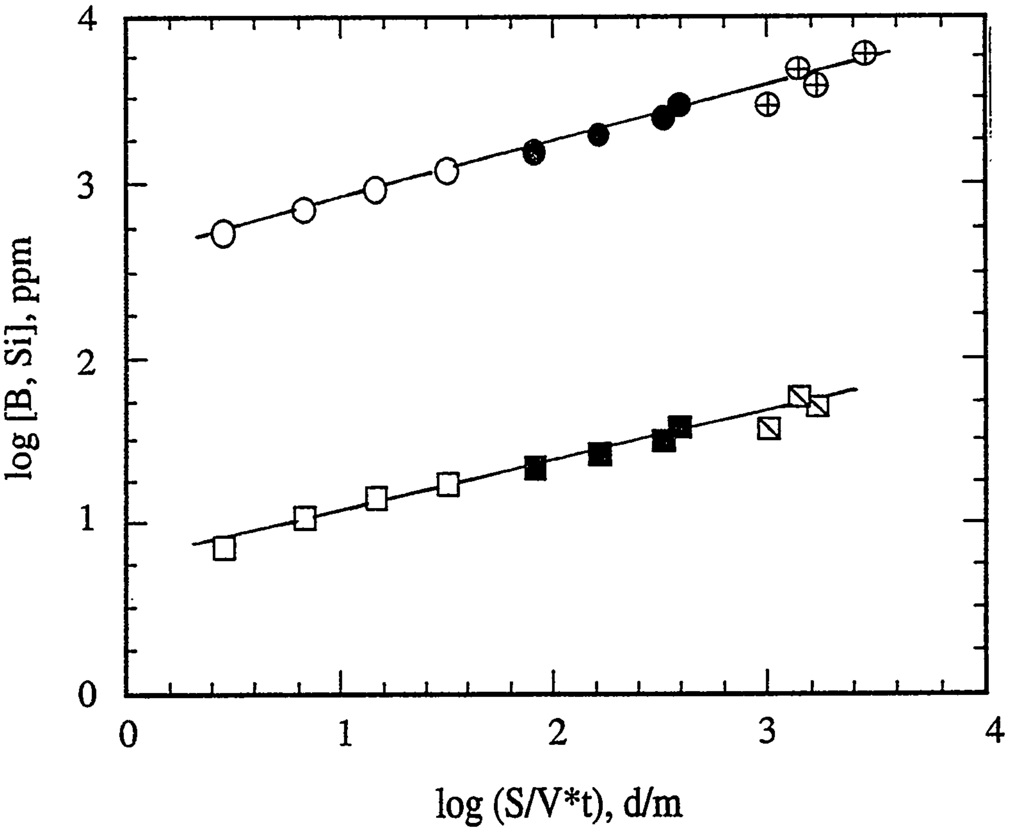

Fig. 2-15. Concentration vs. (S/V)•Time for Release of Boron and Silicon from PNL 76-68 Glass at 90°C (adapted from [PEDERSON-1983b]). (□) Si and (○) B at 1 m^{-1}; (■) Si and (●) B at 10 m^{-1}; (▨) Si and (⊕) B at 100 m^{-1}.

surfaces, which attain a smooth finish as they solidify from the melt. The surface preparation of monolithic samples has been shown to affect glass reactivity early in the testing period to an extent greater than expected from increased surface area alone [BUCKWALTER-1982b; OH-1991]. This effect may be due to the presence of high-energy sites or regions with a high density of $\equiv SiO-Si(OH)_3$ groups. Therefore, differences in reactivity of tests at different S/V ratios may include a component related to the different surface finishes that must be accounted for in the comparison.

Figure 2-16 shows the results from tests of a glass representing Hanford waste, HW-39, using both monoliths polished to a 600-grit finish with carborundum paper and powdered glass of the -100+200 mesh fraction (about 74 to 149 µm screen sizes) [BATES,S.-1989]. All tests were performed at 90°C in deionized water. Monoliths were used in tests at 10 m^{-1} and powders in tests at 530, 2000, and 20,000 m^{-1}. The same mesh-size fraction was used in all powder tests, and the different S/V ratios were achieved by using different mass-of-glass/volume-of-leachant ratios. The surface area of the powders was estimated from the mesh sizes of the test fraction to be about 2×10^{-2} m^2/g. While the actual surface area of the powders is probably different from that quoted due to variations in the grain shapes, the ratios of the tests with powdered glass are expected to be the same. The results of tests at 10, 530, and 2000 m^{-1} (the B concentrations are plotted) can be fitted reasonably well by a single curve, but the results of tests at 20,000 m^{-1} lie well above the data for 2000 m^{-1} at equivalent values of (S/V)•t.

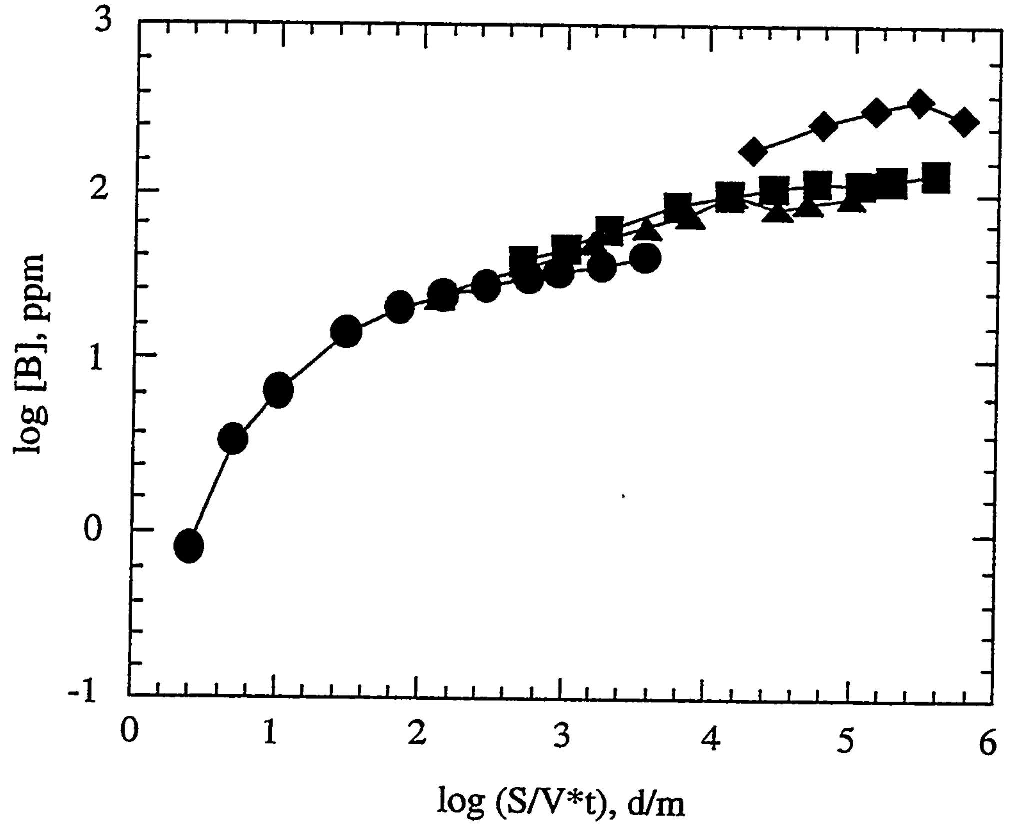

Fig. 2-16. Concentration vs. (S/V)•Time for Release of B from HW-39 Glass at 90°C (adapted from [BATES,S.-1989]) at S/V of (•)10, (▵) 530, (■) 2000, and (♦) 20,000 m^{-1}.

Leach tests using other glass compositions have also shown deviations from (S/V)•t equivalence in tests at high S/V [FILLET-1986; FENG-1990b; VERNAZ-1990; EBERT-1992]. Figure 2-17 shows the results of tests with glasses representative of waste glass to be produced by the DWPF (designated as SRL 131 and SRL 202) at 10 m^{-1} with 600-grit finish monoliths and at 2000 and 20,000 m^{-1} with powdered glass of the -100+200 mesh fraction [EBERT-1993a, -1993b]. Tests at 2000 and 20,000 m^{-1} do not generate similar solutions at equivalent (S/V)•t. The difference in B concentrations at equivalent (S/V)•t is larger for the less durable SRL 131 composition, which contains more alkali metals than the SRL 202 glass. In Fig. 2-17, tests at 20,000 m^{-1} show an upward trend at longer reaction times. This occurs coincidently with the formation of secondary phases, which have been interpreted to affect the solution chemistry and glass reaction rate [VAN ISEGHEM-1988a; EBERT-1992, -1993a]. Such behavior is obviously inconsistent with (S/V)•t scaling.

The deviation from (S/V)•t equivalence has been interpreted as being due to pH effects [VERNAZ-1990; EBERT-1993a] or mass transport effects [FILLET-1986; FENG-1990b; GRAMBOW-1992a; LEMMENS-1992] that are not fully accounted for in Eq. 9. The pH effect observed by Ethridge et al. [ETHRIDGE-1979] at different S/V ratios is also observed in tests with HLW glasses. For example, the leachate pH values (measured at room temperature) for the data in Fig. 2-17 are shown in Fig. 2-18. The differences in the pH curves at different S/V ratio can be attributed to the glass reaction. The initial increase is due to ion-exchange reactions, which dominate the early stages of the glass reaction. The pH rise is faster at higher S/V because of the smaller solution volume available to dilute the hydroxide generated by the reaction. The different pH values attained in tests at different S/V then affect the hydrolysis reactions.

The corrosion of silicate glasses has long been recognized to depend on the pH of the leachant [DOUGLAS-1967; EL-SHAMY-1972a, -1972b]. The pH dependence was thought to result from the dissociation of silicic acid above about pH 9 (90°C), which increases the solubility of Si and thus maintains a larger disequilibrium between the glass and the solution [ALEXANDER-1954].

Recent tests using leachants that were buffered to constant pH values and designed to maintain very low Si concentrations in the leachate to maintain a high reaction affinity have shown the reaction rates of HLW glasses to increase with increasing pH [KNAUSS-1990; ADVOCAT-1991] (see Volume I, Section 3.2). Figure 2-19 shows the results of tests with a soda-borosilicate glass in flowing, buffered leachant solutions. These test conditions maintain the affinity term at a value of one and so eliminate any solubility effects. Above a pH of about 6, the log of the rate of silicic acid release increases linearly with the leachant pH. These data were interpreted using the analytic expression $d[H_4SiO_4]/dt = Sk_f[H^+]^h$, where S is the surface area, k_f is the pH-independent dissolution rate coefficient, $[H^+]$ is the hydrogen ion concentration, and h is a constant [KNAUSS-1990]. (Note that k_f differs from k_+ in Eqs. 9 and 10 in that k_f is pH-independent.) At 70°C, the data between pH values of 5.6 and 13 gave the values $k_f = 10^{-5.1}$ g/m^2d, and h = 0.4. Figure 2-20 shows the release of Si as log(Si, $mole/cm^2/s$) vs. pH from R7T7 glass in static tests performed at very low S/V ratios at 90°C [ADVOCAT-1991]. The log (release rate) of Si is linear at pH values between about 5 and 10, with a slope of about 0.4. These tests suggest that hydroxide is the dominant nucleophile in the hydrolysis reactions over this pH range. The pH dependence of the Si release rate is apparent if the rate-determining step of the hydrolysis reaction is written such that hydroxide is the dominant nucleophile instead of molecular water, as

$$\equiv SiO{-}Si(OH)_3 + OH^- \rightarrow \equiv SiO^- + H_4SiO_4. \tag{11}$$

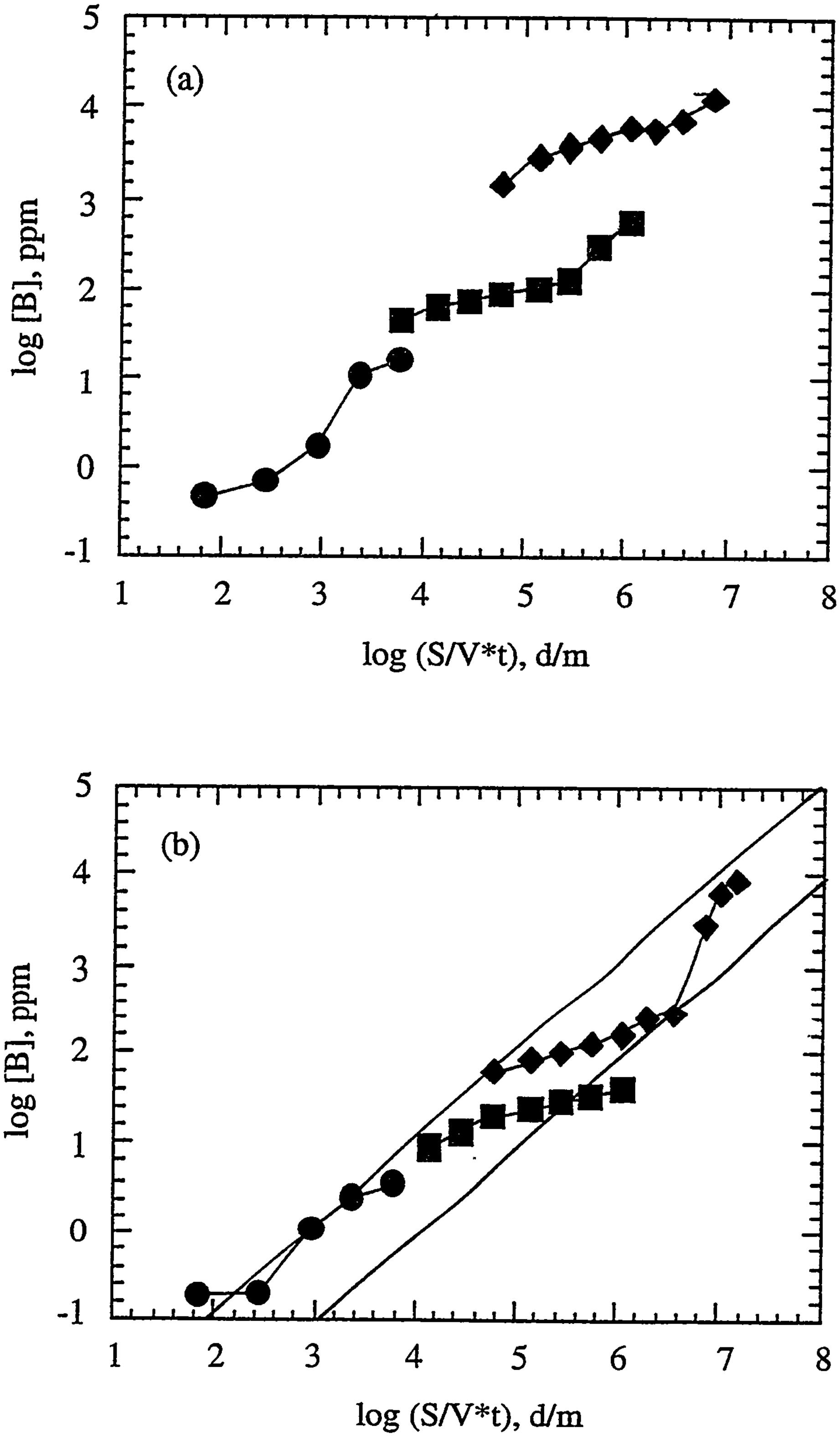

Fig. 2-17. Concentration vs. (S/V)•Time for Release of B from (a) SRL 131 Glass and (b) SRL 202 Glass at 90°C at (•) 10, (■) 2000, and (♦) 20,000 m^{-1} (adapted from [EBERT-1993b]).

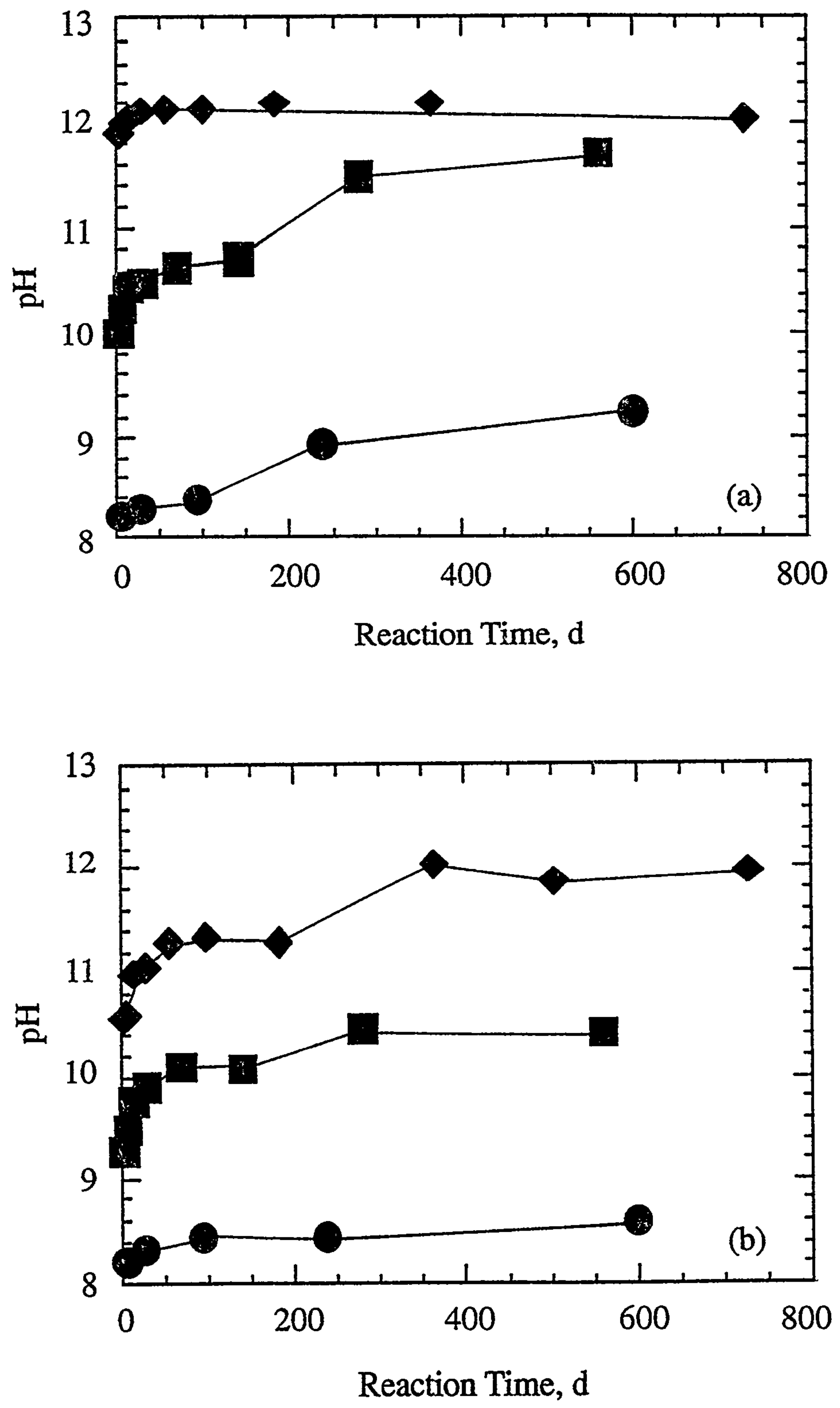

Fig. 2-18. Leachate pH Values (25°C) vs. Reaction Time for (a) SRL 131 Glass and (b) SRL 202 Glass Reacted at 90°C at (•) 10, (■) 2000, and (♦) 20,000 m^{-1} (adapted from [EBERT-1993b]).

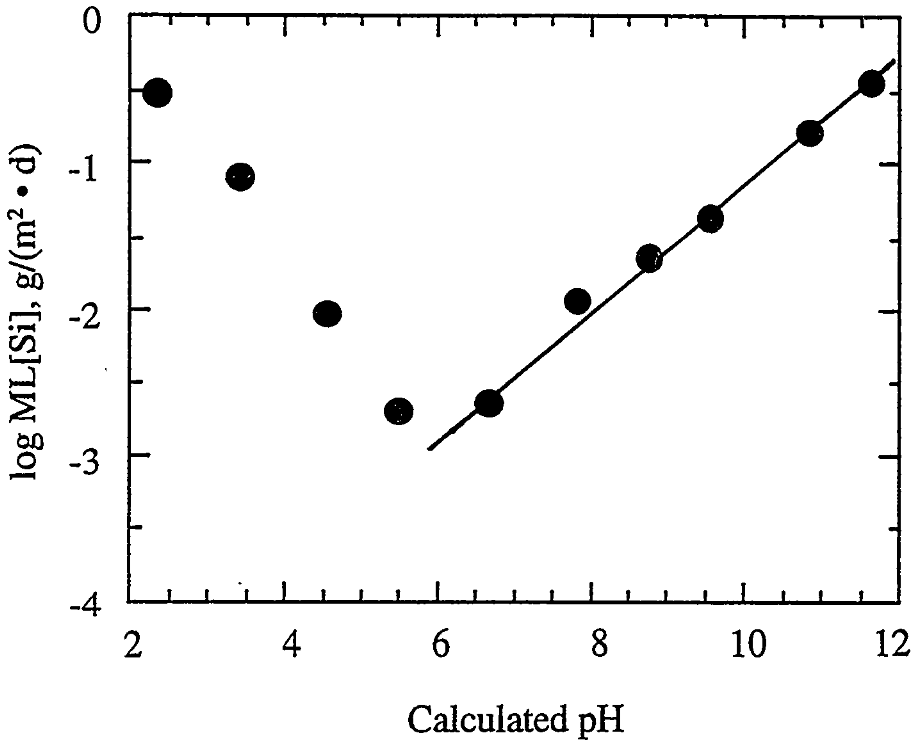

Fig. 2-19. Dissolution Kinetics of a Simple Analog Glass as a Function of Leachant pH at 70° (adapted from [KNAUSS-1990]).

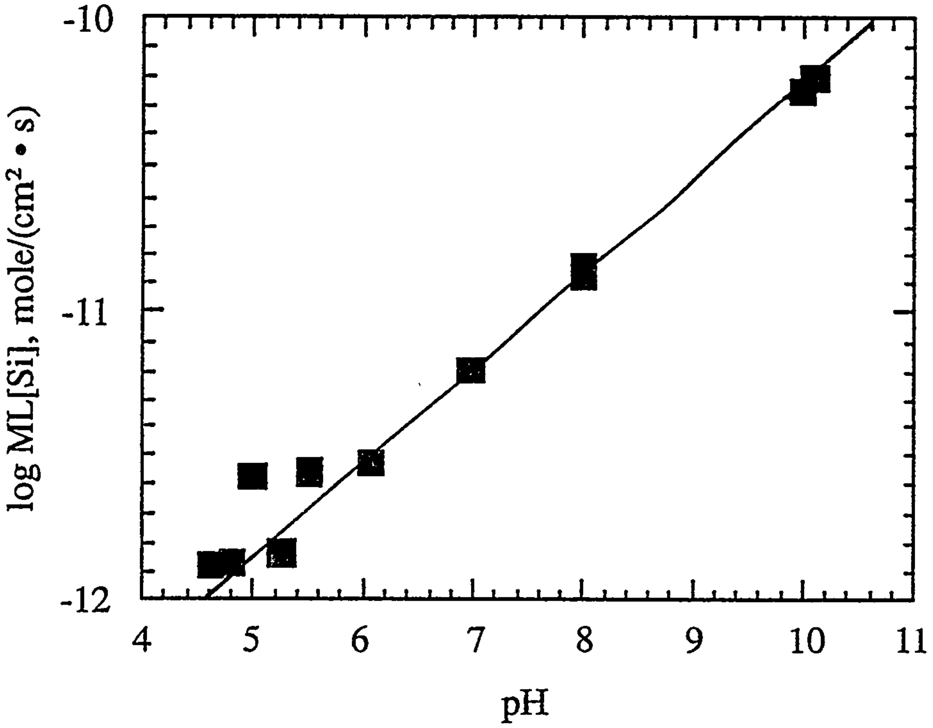

Fig. 2-20. Hydrolysis of R7T7 Nuclear Waste Glass in Dilute Media as a Function of Leachant pH at 90°C (adapted from [ADVOCAT-1991]).

Based on Eq. 11, the reaction rate term will have a pH dependence, as

$$\frac{d[H_4SiO_4]}{dt} = \frac{S}{V} k_f [OH^-]^h \left(1 - \frac{[H_4SiO_4]}{[H_4SiO_4]_{sat}}\right) \qquad (12)$$

In this expression, the pH dependence of the rate coefficient is written explicitly through the $[OH^-]^h$ term. The order of the rate dependence with respect to hydroxide is different than one because the glass corrosion is more complicated than the simple reaction given in Eq. 11.

Integration of Eq. 12 to compare results of static leach tests requires knowledge of the time dependence of the hydroxide concentration, which is affected by ion-exchange reactions, possible precipitation of metal hydroxides and other secondary phases, and buffering due to dissociation of silicic and boric acids. Thus, a general expression equivalent to Eq. 10 cannot be written, although Eq. 12 can be solved numerically by coupling it with geochemical codes. Qualitatively, the result of the pH dependency in Eq. 12 is that a time-dependent hydroxide concentration term appears in the argument of the exponent, which must then be included in the scaling correlation variable [EBERT-1993a].

The thicker layers formed in tests at low S/V [PEDERSON-1983a] might be expected to affect mass transport to a greater degree than would the thinner layers formed in tests at higher S/V. Some workers [FILLET-1986; FENG-1990b; LEMMENS-1992] have suggested that the diffusion of soluble reaction products or water [GRAMBOW-1992a] is responsible for deviations from (S/V)•t equivalence. A rate expression for diffusion-limited dissolution yielded a correlation variable of $(S/V)\cdot(t)^{1/2}$ [MACHIELS-1983], and some test results show a better correlation with $(S/V)\cdot(t)^{1/2}$ than with (S/V)•t [GRAMBOW-1992; LEMMENS-1992]. The long-term rates observed in some tests are similar to water diffusion rates measured in other glasses [GRAMBOW-1992], while other tests have shown that higher release rates occur from samples having the thickest reaction layers [VERNAZ-1990; EBERT-1993c]. Both the higher pH values and the differences in layer thickness may lead to the positive deviation from (S/V)•t at high S/V that has been observed experimentally, perhaps depending on the glass composition and test conditions used. It is also possible that different rate-controlling reaction steps control the corrosion observed under different test conditions. These effects preclude the extrapolation of short-term test results to long times without properly accounting for differences in both the solution chemistry and the surface layer as the reaction proceeds.

2.3.2 Effects of the Flow Rate in Dynamic Leach Tests

Tests with flowing leachant or tests wherein a volume of leachate is periodically replaced with fresh leachant provide continual dilution of the leachate solution. Because the solution composition is understood to control the glass reaction (see Volume I, Section 3.2), changes in the leachate under dynamic test conditions are expected to affect the glass reaction rate. The increase in silicic acid concentration in solution due to glass dissolution is counteracted by the removal of silicic acid due to leachant removal through flow. The reaction will maintain a high rate if the silicic acid concentration at the glass surface is kept below its saturation value. Figure 2-21 shows the effect of leachant flow rate on the glass reaction rate in tests with SRL 131 type glass reacted in deionized water at 90°C [MENDEL-1984, pg. 1.20; ADIGA-1985]. As seen in Fig. 2-21a, a flow rate of 1.0 mL/h is required

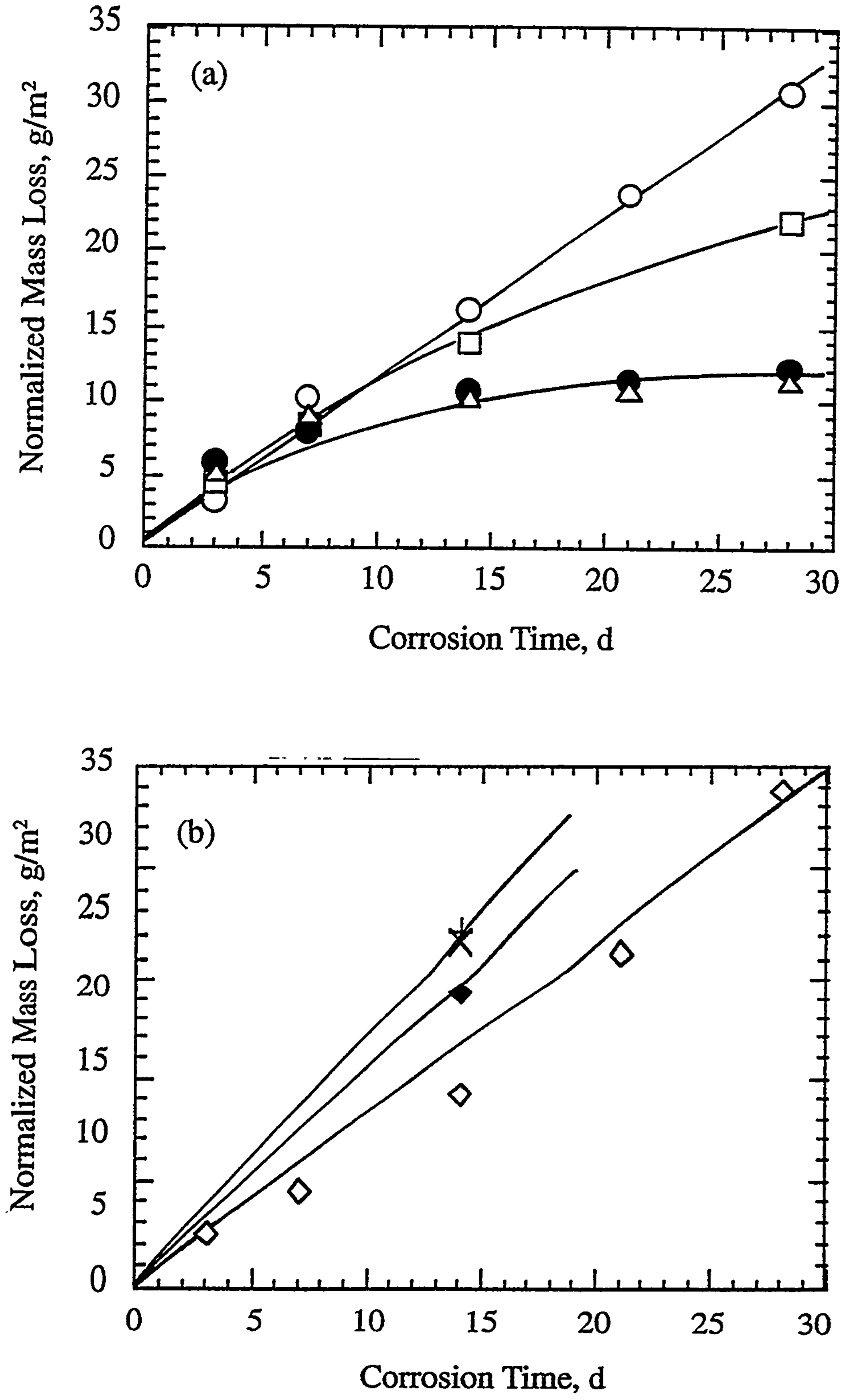

Fig. 2-21. Mass Loss vs. Corrosion Time for SRL 131 Glass Reacted at 90°C at Various Flow Rates (adapted from [ADIGA-1985]). (a) (Δ) Static, (•) 0.1 mL/h, (□) 0.5 mL/h, (○) 1.0 mL/h, and (b) (◊) 10 mL/h, (♦) 25 mL/h, (+) 50 mL/h, (x) 100 mL/h.

to maintain a constant, steady-state corrosion rate, although, as seen in Fig. 2-21b, the maximum rate of glass reaction is not achieved until the flow rate is increased to 50 mL/h. The forward rate based on mass loss is about 2.5 g/m^2/day.

The effect of the leachant flow rate on the glass reaction rate can be quantified in a conservation of mass expression [APTED-1985; HENCH-1986c; MACEDO-1982; MACHIELS-1983]. Consider the reaction to occur in a well-mixed reactor with equal flow rates into and out of the cell containing the glass. The silicic acid concentration in the reactor will include that generated by the glass reaction, plus any silicic acid in the added leachant, less that removed from the system due to flow or leachate sampling. This can be expressed mathematically as

$$\frac{d[H_4SiO_4]}{dt} = \frac{S}{V} k_f [OH^-]^h \left(1 - \frac{[H_4SiO_4]}{[H_4SiO_4]_{sat}}\right) - \frac{f\,[H_4SiO_4]}{V} \qquad \textbf{(13)}$$

where $[H_4SiO_4]$ represents the silicic acid concentration in the leachate, $[H_4SiO_4]_{sat}$ is the "saturation" concentration of silicic acid, t is time, S is surface area, V is reactor cell volume, and f is flow rate. The first term on the right-hand side of the equation accounts for the release of silicic acid from the glass (see Eq. 12) and the second term for the removal of silicic acid from the system due to flow. This expression does not account for effects of diffusion in the solution or in surface layers (see Volume I, Section 3.3.2.2).

Under constant flow conditions, a steady state may be attained wherein the silicic acid concentration in the cell (and at the glass surface) remains constant. The steady-state silicic acid concentration, which is written as $[H_4SiO_4]_{ss}$, can be determined by setting $(d[H_4SiO_4] / dt) = 0$ in Eq. 13 and solving for $[H_4SiO_4]$. By substituting the expression for $[H_4SiO_4]_{ss}$ into the rate equation for glass reaction, Eq. 12, the rate of glass reaction necessary to maintain steady-state conditions can be expressed as a function of the flow rate as

$$\frac{dn(H_4SiO_4)_{ss}}{dt} = \frac{S\, k_f [OH^-]^h f}{\dfrac{S}{[H_4SiO_4]_{sat}} k_f [OH^-]^h + f} \qquad \textbf{(14)}$$

where $n(H_4SiO_4)_{ss}$ is the number of moles of silicic acid released from the glass under steady-state conditions. Equation 14 can be simplified in the limits of high and low flow rates. At high flow rates, where $f >> (S/[H_4SiO_4]_{sat})k_f[OH^-]^h$,

$$\frac{dn(H_4SiO_4)_{ss}}{dt} = S\, k_f [OH^-]^h \qquad \textbf{(15)}$$

and the rate of glass reaction is independent of the flow rate. At low flow rates, where $(S/[H_4SiO_4]_{sat})k_f[OH^-]^h >> f$, the reaction rate is

$$\frac{dn(H_4SiO_4)_{ss}}{dt} = [H_4SiO_4]_{sat}\, f \tag{16}$$

and the rate of glass reaction is proportional to the flow rate. From Eq. 15, a sufficiently high flow rate exists where the glass reacts at its (maximum) forward rate, and further increases in flow will not affect the glass reaction rate. These conditions have been used to measure the forward reaction rates of HLW glasses [KNAUSS-1990]. Decreasing the flow rate will result in an increase in the silicic acid concentration and a decrease in the glass reaction rate until a new steady state is achieved [BARKATT-1984a]. The dependence of the reaction rate on flow is shown in the results of leachate replacement tests. These test results, as seen in Fig. 2-22, show the behavior predicted by Eqs. 15 and 16 at high and moderate effective flow rates, even though the replacement tests only approximate low leachant flow rates.

The influence of flow rate on the glass reaction can be summarized as follows. At high flow rates, the reaction proceeds at a maximum rate that depends on the leachate composition, pH, and the reaction temperature but is independent of the flow rate. At intermediate flow rates, the reaction rate is proportional to the flow rate and depends on the steady-state solution composition at the glass surface. At very low flow rates, a steady-state composition is not achieved, and the reaction rate decreases with time as the solution becomes more concentrated; this occurs at flow rates below about 1 mL/h in Fig. 2-21a where a constant reaction rate is not achieved. The rate of concentration change is only weakly affected by the flow rate at very low flow rates, and tests at flow rates less than 0.1 mL/h are indistinguishable from static tests (Fig. 2-21a). The generation of surface layers may present a transport barrier and affect the corrosion rate under some test conditions. An additional term may be added to Eq. 13 to account for this effect, such as that added in the Grambow model (see Volume I, Section 3.3.2.2).

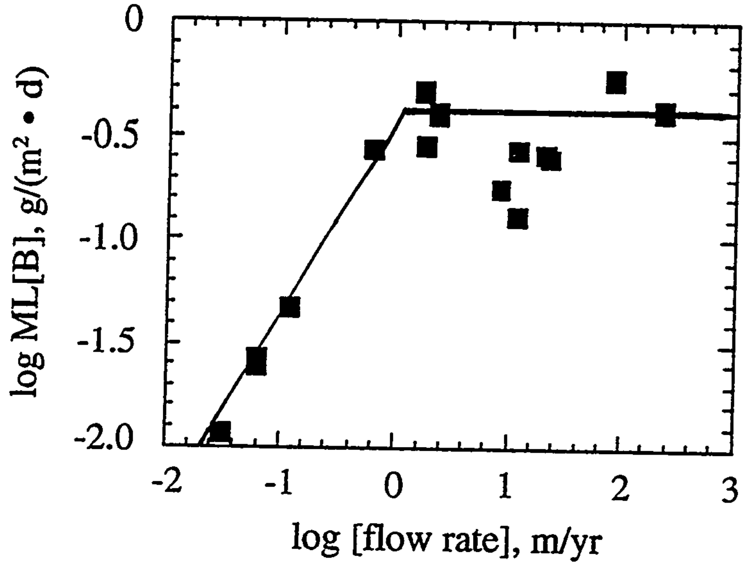

Fig. 2-22. Boron Release from SRL TDS-131 as a Function of Flow Rate (adapted from [BARKATT-1984a]).

2.3.3 Results from Tests at Very High S/V Ratios

Because the solution composition controls the glass reaction rate and the S/V ratio of a static test determines the extent of dilution of the solution, the S/V used in a test provides a valuable means of highlighting the glass reactivity under various solution conditions. By maintaining dilute solutions at very low S/V in static tests or in dynamic tests, the reaction affinity can be kept near one and the forward reaction rate determined. Conversely, by performing tests at very high S/V, the reactivities of glasses in undiluted leachate solutions where the reaction affinity is very small can be characterized. Although they may not be quantitatively related to other laboratory tests because of the high pH values that are achieved, tests at very high S/V ratios[3] provide valuable insights into glass behavior in highly concentrated solutions, such as those that might exist near the waste form in a repository due to glass corrosion itself.

Different experimental techniques have been used to achieve very high S/V ratios. Pederson et al. [PEDERSON-1983a] utilized wire spacers to separate glass monoliths and produce a plane capillary to achieve an S/V ratio of about 1600 m^{-1}. This technique produced reacted glass that could be analyzed in detail, but the leachate analysis was limited to a pH measurement. Powdered glass is used routinely to achieve high S/V ratios. These tests provide for leachate analyses and solids analysis of the reacted glass, although the very large number of reacted grains complicates the cataloging of all secondary phases that may be generated. Very high S/V ratios have also been attained in vapor at elevated temperatures [SANDERS-1973a; BATES-1982a, -1984a]. In the vapor environment, reaction occurs in a thin film of condensed water where highly concentrated solutions are generated after very little glass has reacted [EBERT-1991b]. Secondary phases that form in the leachate film remain on the sample surface, where they can be readily identified and catalogued. Leachate analyses cannot be performed with this method because the water evaporates during test termination; however, residual salts can be redissolved and analyzed [EBERT-1991b].

The results of tests at very high S/V ratios are consistent with the effects of S/V predicted by Eq. 12, namely, that highly concentrated solutions are quickly attained and the reaction rate becomes very low. Because glass is metastable and cannot equilibrate with the leachate, a "residual reaction rate" is present even when the solution becomes saturated [GRAMBOW-1984a; FREUDE-1985]. Continued glass reaction under saturated conditions (where the affinity for Eq. 11 becomes small) occurs because water diffusion and ion-exchange reactions may continue under these conditions, even though the reaction rate may be immeasurably low [ADVOCAT-1990; PETIT-1990b; GRAMBOW-1992]. The low rate attained under saturated conditions does not necessarily represent the long-term reaction rate. An increase in the glass reaction rate has been observed in tests where secondary phases have formed after long reaction times [VAN ISEGHEM-1988a; EBERT-1992, -1993c]. The sudden increases in B concentration in Fig. 2-17 are, for example, indicative of an increase in the reaction rate coincident with secondary phase formation. Such increases are consistent with the model of glass reaction and Eq. 12 in that secondary phase formation affects the solution chemistry, which will result in an increased reaction rate if the solubility limit of silicic acid ($[H_4SiO_4]$ in Eq. 12) is maintained at a value less than $[H_4SiO_4]_{sat}$ [BOURCIER-1990]. Enhanced reaction is also observed in the presence of clays [GODON-1990], which remove Si from solution and so also affect the solution chemistry. Which solution species affect the glass corrosion rate is not yet fully understood. Although silicic acid has been identified as the dominant species affecting the reaction [GRAMBOW-1985], recent results suggest that other solution species may also affect the observed

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[3] Very high S/V refers to tests performed under conditions where the leachate volume is too small to be completely analyzed.

reaction rates [PETIT-1990b; BOURCIER-1992]. The relative importance of the silicic acid concentration on the glass corrosion rate may depend on the glass composition and the reaction conditions.

2.3.4 Experimental Measurement of Glass Corrosion Rates

The release rates of glass components measured in both static and dynamic leach tests and the models they support provide valuable insight into the behavior of high-level waste glasses expected under long-term storage in a waste repository. From the discussion in previous sections, the release of glass components is expected to slow as solution concentrations increase, with the silicic acid concentration and the pH usually assumed to be the dominant factors controlling the corrosion rate. Based on the model of solution control of the corrosion rate, two characteristic rates can be defined corresponding to infinite dilution and silicon saturation conditions. A "forward reaction rate" can be measured under highly dilute conditions and a "saturation rate" can be measured under "saturated" conditions. Of course, the saturated conditions depend on the controlling solid phase(s). Experimental evidence suggests that the rate under "saturated" conditions remains nonzero, although the reason is uncertain. It has been suggested that the continued reaction is due to ion exchange reactions [VAN ISEGHEM-1992] or the diffusion of water into the glass [GRAMBOW-1992a], which is not strongly affected by the "saturated" solution. The model also accounts for the formation of secondary phases which affect the solution concentration of silicic acid (and other glass components) and the pH. Formation of these phases will also affect the corrosion rate. Some models include a term to account for mass transport through surface layers formed during glass reaction [GRAMBOW-1985, -1987]. Such a term will not be considered here.

A simple form of the rate equation utilized in current simulations of glass corrosion which can be written similar to Eq. 12 as

$$\frac{d[B]}{dt} = \frac{S}{V} k_f [OH^-]^h \left(1 - \frac{[H_4SiO_4]}{[H_4SiO_4]_{sat}} \right) + R_\infty \qquad (17)$$

where the rate is expressed in terms of the solution concentration of boron rather than silicic acid (see Section 1.2) and the term R_∞ has been added to account for the nonzero reaction rate under "saturated" conditions. If secondary phases form to limit the silicic acid concentration in solution such that the affinity term remains nonzero, then the rate will be determined by the first term on the right hand side. Otherwise, the first term will approach zero and the long-term rate will be given by R_∞. Solution of Eq. 17 requires knowledge of k_f (note: the numerical value of k_f differs from that in Eq. 12 because the B and Si concentrations involved are not normalized), h, $[H_4SiO_4]_{sat}$, and R_∞. The values of these parameters can be determined experimentally either by regression to the test data or by conducting separate experiments designed to highlight specific parameters. A pH-dependent rate coefficient k_+ is often used, where $k_+ = k_f[OH^-]^h$, so that k_f and h are not determined separately. The term R_∞ is usually treated as an ad hoc corrective parameter to improve the fit of the equation to the long-term data.

These reaction parameters can be determined using the results of static leach tests in a plot of the corrosion rate against the silicic acid activity (or concentration) where k_+ is the rate when the silicic acid activity is zero. R_∞ and the saturation concentration are estimated from the rates measured at high activities [GRAMBOW-1987]. Scatter in test data lead to large uncertainties in the regressed values in this approach.

Two limiting solutions can be defined with regard to Eq. 17: highly dilute solutions where the term in parentheses is near one ($[H_4SiO_4] \approx 0$), and highly concentrated or "saturated" solutions where the term in parentheses is near zero ($[H_4SiO_4] \approx [H_4SiO_4]_{sat}$). Under the limit where $[H_4SiO_4] \rightarrow 0$, the rate equation can be written as

$$\frac{d[B]}{dt} = \frac{S}{V} \{k_+ + R_\infty\} \qquad \textbf{(18)}$$

and under the limit where $[H_4SiO_4] \rightarrow [H_4SiO_4]_{sat}$, the rate equation can be written as

$$\frac{d[B]}{dt} = \left(\frac{S}{V}\right) R_\infty \qquad \textbf{(19)}$$

Tests performed at very low values of (S/V)t maintain dilute solutions and are expected to approach a maximum rate as (S/V)t decreases, which represents the forward reaction rate. Tests at increasing (S/V)t will approach a minimum rate at increasing values of (S/V)t, which generate "saturated" solutions. The minimum rate represents the reaction rate under "saturated" conditions.

High values of (S/V)t can be attained either by performing tests at high S/V or for long time periods. However, as described earlier in Section 2.3.1, higher solution pH values may result in faster corrosion in tests at high S/V. The effects of the pH and the silicic acid concentration on the measured reaction rate cannot be separated using these test data.

Under conditions where the glass corrodes at a constant rate, data in a plot of log[B] versus log{(S/V)t} with fall on a line with a slope = 1 [BUNNELL-1986; STRACHAN-1990, pp. 3.9-3.10; EBERT-1993b]. From Eqs. 18 and 19, this is expected to occur at low values of (S/V)t, where the line corresponds to the forward rate and the y-intercept of that line, that is, the value at log{(S/V)t} = 0, gives the value of $\log\{k_+ + R_\infty\}$. The data are also expected to fall on a line of slope 1 at high values of (S/V)t, and the y-intercept of that line gives the value of $\log\{R_\infty\}$. Note that the values of k_+ and R_∞ determined from the data will both depend on the solution pH of the tests under the limiting conditions of low and high (S/V)t, respectively.

Which step or steps control the corrosion rate under "saturated" conditions is not presently well-understood. Continued reaction may be due to the ion exchange reactions [VAN ISEGHEM-1992], water diffusion [GRAMBOW-1992a], or even to network hydrolysis reactions since thermodynamic equilibrium between the glass and solution cannot be achieved. More work is clearly needed to elucidate the nature of glass corrosion in highly concentrated solutions and the effects of the temperature, solution composition, pH, etc. on the reaction rate. Currently, the reaction rate under "saturated" conditions can only be regressed from experimental data from tests which approach a minimal rate.

High values of (S/V)t can be attained either by performing tests at high S/V or for long time periods. However, as described earlier in Section 2.3.1, higher solution pH values may result in faster corrosion in tests at high S/V. With regard to Eq. 19, tests at higher S/V may have greater values of k_+ due to the higher pH values that are attained. The effects of the pH and the silicic acid concentration on the measured reaction rate cannot be separated using these test data.

Application of the technique is demonstrated using the data presented in Fig. 2-17b where lines with slopes of one have been drawn through data for SRL 202 glass reacted at 20,000 m^{-1}. The line with a slope of one drawn through the data point from the test run for the shortest time, which was three days, yields a y-intercept of log{[B]} = -3. Thus, about 1 x 10^{-3} g of boron per m^3 of solution (units of [B] are ppm) has been released after a reaction progress of (S/V)t = 1 day/m. The average release rate over the first three days is therefore 1 x 10^{-3} g B/m^2/day. Since the weight fraction of boron in SRL 202 glass is 0.025 (the composition is given in Volume I, Appendix A and [BATES-1993, pg. 4]), the rate of glass corrosion given in the units of g glass/m^2/day is (1 x 10^{-3} g B/m^2/day) x (1 g glass/0.025 g B), which is about 0.04 g glass/m^2/day. Note that this is the average rate over three days and that the solution pH has increased from about 8.2 to about 10.5 over this period. This value can be compared to the corrosion rate measured in a flow-through experiment using a similar glass [KNAUSS-1990], which is predicted to be about 0.05 g glass/m^2/day at 90°C and at a pH of 10.5, and 0.005 at a pH of 8.2 based on the measured temperature and pH dependencies. The agreement between forward rates measured using the data in Fig. 2-17b and that predicted from flow-through tests is quite good. Similar treatment using data obtained for static tests run at 2000 m^{-1} gives a forward rate of 0.025 g glass/m^2/day based on the data for 3 days of reaction. The lower rate measured in tests at 2000 m^{-1} probably results from the lower pH attained in these tests.

The saturation rate attained in the experiments with SRL 202 glass in Fig. 2-17b at 20,000 m^{-1} occurred after about 180 days (at log[(S/V)t] = 6.56), where the line of slope one drawn through this point gave a rate of 0.0025 g glass/m^2/day, which is 16 times lower than the rate after three days of reaction. The observed decrease in the rate between three and 180 days is due to the saturation of the solution, although the higher solution pH after 180 days of reaction compared to the pH attained after three days of reaction (about 11.2 compared to about 10.5) may have accelerated the reaction slightly.

Tests run longer than 180 days yield reaction rates that are higher than that measured after 180 days. The increase is due in part to the higher pH values (about 12) that are reached in tests run longer than 180 days. The pH is expected to increase the value of k_+ and accelerate the reaction. The cause of the pH increase is uncertain, but may involve the formation of secondary phases [EBERT-1991a, -1991b, -1993c; VAN ISEGHEM-1993]. The observed increase in the corrosion rate indicates that the "saturation rate" does not represent the long-term corrosion rate for this glass under these conditions, and that the long-term rate may be significantly higher than the "saturation rate." Notice that the lowest rate observed in tests performed at 2000 m^{-1} can be seen in Fig. 2-17b to be lower than the lowest rate attained in tests performed at 20,000 m^{-1}. (Data points for tests at 2000 m^{-1} run for large (S/V)t lie to the right of the line of slope one drawn through the data point showing the lowest rate in tests at 20,000 m^{-1}.) This implies that the solution is not yet saturated after reacting for 180 days at 20,000 m^{-1}, and that the first term in Eq. 17 is still dominating the observed corrosion rate. It also implies that the silicic acid concentration is being maintained below its initial saturation value due to secondary phase formation, and the reaction rate remains greater than R_∞. In fact, the reaction rate has increased to near the rate observed after only three days of reaction. A similar increase in the corrosion rate at long reaction time has been observed in other tests [FENG-1993b].

The value of $[H_4SiO_4]_{sat}$ can also be determined from experimental data when the minimum rate occurs, but the accuracy is limited by the sensitivity of the silicon solubility to the pH above about pH 9 due to dissociation. Values are usually found to vary slightly for different glass and leachant compositions, but are typically on the order of 1×10^{-3} M, and are intermediate between the solubilities of quartz and amorphous silica [GRAMBOW-1988, pg. 25; GRAMBOW-1992b; VERNAZ-1990; ADVOCAT-1990; DELAGE-1992].

In a slightly different approach, Bourcier has represented the reaction affinity in terms of the alteration layer which forms on the reacted glass instead of only silicon. The silicic acid concentration in Eq. 17 is replaced by the activity product of components which remain in the layer, while the saturation value is computed using the solubilities of phases modelled to comprise the layer [BOURCIER-1990]. The layer compositions are measured experimentally, but are well approximated by simply excluding soluble alkali metals and boron from the glass composition. Layers typically include silicon, aluminum, iron, calcium, and magnesium. This approach identifies the "saturation" controlling phase as the alteration layer and couples the glass composition to the "saturation" composition.

Reaction rates determined using the data in Fig. 2-17 by the method described above are presented in Table 2-5 with rates determined by others using static or dynamic test data for several glass compositions. Several observations can be made comparing the results. The forward reaction rates are generally between 1 and 2 g glass/m^2/day at 90°C, although some measurements yield much lower rates. The forward rates measured under dynamic conditions are probably more accurate than those measured under static conditions due to the buildup of reaction products in the leachates of static tests. The buildup of reaction products in static tests and in dynamic tests at low flow rates reduces the reaction rate, such that the average rates measured over even short time periods represent lower limits of the forward rates.

The rates measured under "saturated" conditions are typically two to three orders of magnitude smaller than the forward reaction rates. However, "saturated" rates measured for the same glass reacted in different leachants or at different S/V also show differences of a factor of ten or more between measurements. This may indicate that a unique "saturation" rate may not exist for different glass compositions [VERNAZ-1990] or that the solution can have more than one "saturation level" associated with the formation of different secondary phases. In addition, the corrosion rate may increase as more stable secondary phases form over very long reaction times [EBERT-1993c; FENG-1993b].

2.3.5 Repository Relevance

In a repository, both the accessible glass surface area and the groundwater volume will likely change over the storage time, and the repository cannot be represented by a unique S/V ratio. Nevertheless, insight gained through laboratory tests at different S/V ratios regarding the effects of solution chemistry on glass corrosion is directly applicable to assessments of the long-time performance of borosilicate glass waste forms. The following discussion is limited to the glass and the fluid contacting the glass, as described in Volume I, Section 1.2.

The surface area of HLW glass that is accessible to groundwater in a repository setting will be determined, in part, by the extent of cracking of the poured glass due to thermal and mechanical stresses [SLATE-1978; SMITH-1981] (see Section 2.1). Peters et al. [PETERS-1981a] measured the surface area of glass in DWPF canisters that were cooled over a period of 50 hours and found that the

Table 2-5. Experimentally Determined Reaction Rates at 90°C, in g glass/m^2/day

Glass/Leachant	S/V (m^{-1})	Forward Rate	Saturation Rate	Reference
Static Tests				
PNL 76-68/DIW	2000	1.6	0.08[a]	A
SRL 165/DIW	2000	0.80	0.024[a]	A
EMS-11/DIW	2000	0.083	0.0016[a]	A
JSS-A/DIW	10[b]	1.5	0.0025	B
PNL 76-68/DIW	10[b]	1.8	0.0075	B
SRL 131/DIW	10[b]	3.0	0.033	B
SRL 131/J-13[c]	10	0.14		C
SRL 131/J-13	2000	0.24	0.021	C
SRL 131/J-13	20,000	0.84	0.053	C
SRL 202/J-13	10	0.10		C
SRL 202/J-13	2000	0.025	0.0016	C
SRL 202/J-13	20,000	0.04	0.0025	C
R7T7/DIW	5	4.9 (100°C)		D
R7T7/DIW	50		0.0083	E
R7T7/Volvic[d]	50		0.0133	E
R7T7/DIW	400		0.0045	E
R7T7/Volvic	400		0.025	E
R7T7/Volvic	2000		0.0006	E
R7T7/Volvic	8000		0.0006	E
R7T7/Volvic	20,000		<0.0001	E
MW/DIW	1320	1.1	0.01	F
Dynamic Tests				
SRL 202/pH 7 Buffer		0.28 (80°C)		G
SRL 165[e]/pH 10.5 Buffer		0.05[a]		H
SRL 165[e]/pH 10 Buffer		0.08 (70°C)		I
R7T7/DIW		1.03		J
SRL 131/DIW		2.5		K

[a] Estimated.

[b] Values determined from results of both static and dynamic tests.

[c] Tuff groundwater. Major components are 45 ppm Si, 55 ppm Na, and 120 ppm HCO$_3^-$.

[d] Granite groundwater. Major components are 11 ppm Si, 9.8 ppm Ca, 9.2 ppm Na, and 66 ppm HCO$_3^-$.

[e] Analog glass without iron.

References

A = [BUNNELL-1986], B = [GRAMBOW-1988], C = [EBERT-1993b], D = [ADVOCAT-1990], E = [VERNAZ-1990], F = [CURTI-1991, pg. 25], G = [McGRAIL-1991], H = estimated from the results of [KNAUSS-1990], I = [BATES-1992c] rate based on sodium release, J = [DELAGE-1991] rate based on boron release, and K = [ADIGA-1985] rate based on mass loss.

surface area increased by a factor of about 18 compared with the surface area of the uncracked monolith in the canister. Similar fracturing of DWPF waste was observed after burial for about three years [MOLECKE-1993]. Baxter has estimated a factor of 25 to be a conservative representation of the increase in glass surface area due to cracking [BAXTER-1983]. Mechanical stress may occur during routine handling or accidental impacts. The results of 9-m drop tests suggest an increase in the total surface area by a factor about 27 [SMITH-1975].

Perez and Westsik [PEREZ-1981] studied the contribution of variously sized artificial cracks to glass leaching and found that the extent of reaction did not increase when tight cracks were present. They interpreted their results as indicating that some fractures were too narrow for water to access the glass surfaces within these cracks. However, it is expected that the small fluid volumes that may exist within a crack will become saturated very quickly such that reaction within the crack will be insignificant compared to reaction at free surfaces under low S/V conditions. The contribution from surfaces within cracks may become more significant under very high S/V conditions. In another study, sections of full-scale canistered waste were leached under MCC-1 type conditions in order to compare the corrosion of a full-sized sample to that of a laboratory-scale sample under MCC-1 conditions [BICKFORD-1987]. The combined effects of thermal cracking, scaleup, and surface roughness from saw cuts on the full-sized section resulted in only a factor of three increase in the reaction rate relative to tests on smaller glass monoliths prepared in the laboratory. The observed increase was attributed primarily to the rougher finish of the saw-cut sections removed for testing [BICKFORD-1987]. Any additional surface area produced by thermal cracking at the glass/canister interface had a negligible effect on the total extent of reaction.

The volume of water in contact with the glass at any time will depend on the groundwater flow through the repository. For example, one limiting case may involve the filling of a breached glass canister such that the entire air volume of the canister becomes filled with water. The S/V of the system within the canister will continually decrease as the void volume is filled until a "minimum" S/V is attained when the canister is completely filled. The precise S/V ratio will then depend on the glass and void volumes of the canister and the extent of cracking of the glass. If the water in the canister can be refreshed after filling, then the effective S/V will be even lower.

2.3.6 Summary

- The effects of both the S/V used in static tests and the flow rate used in dynamic tests on the glass reactivity can be described in terms of their effect on the solution chemistry of the fluid (specifically the silicic acid concentration and the pH) in contact with the reacting glass.

- Current corrosion models identify the hydrolysis of silicon-oxygen bonds at the glass surface to release silicic acid as the reaction step controlling the long-term glass corrosion. The rate of this reaction is affected by the silicic acid concentration in the solution and the solution pH.

- The solution chemistry is affected by the S/V used in static leach tests. Tests at high S/V generate more concentrated solutions after a given reaction time than tests at lower S/V.

- Schemes utilizing the S/V as a means of accelerating the reaction progress must account for the higher pH values that are attained at high S/V tests and for other effects, such as secondary phase formation.

- Tests in flowing or periodically refreshed leachant solutions inhibit the buildup of reaction products in the solution contacting the glass, which in turn affects the glass reaction rate.

  - At moderate flow rates, the glass reaction rate responds to changes in the solution chemistry due to changes in the flow rate to maintain steady-state solution concentrations of those glass components controlling the reaction rate.

  - As the flow rate increases, reaction products are more quickly removed, so the fluid in contact with the glass becomes more dilute and the glass reaction rate increases. A maximum reaction rate is observed at high flow rates at which the glass reacts at its forward rate.

  - As the flow rate decreases, the fluid in contact with the glass may become more concentrated as the glass reacts and the glass reaction rate will decrease. At very low flow rates, the system may be indistinguishable from a static system and the glass reaction rate may become controlled by the dilution of released glass components.

- The rate may increase in either static or dynamic tests due to the effects of secondary phase formation or other materials interactions on the solution chemistry.

2.4 Temperature Effects

The mechanisms for the aqueous corrosion of HLW glass typically comprise the complex interaction of corrosion processes, each of which consist of one or more chemical reaction and mass transport steps (see Table 1-1). Steps in the corrosion process include molecular water diffusion and secondary mineral formation [e.g., DRAN-1988; ABRAJANO-1989, -1990b; PETIT-1990c; YANG-1990]. A number of studies have investigated the temperature dependence of these individual reaction processes. Temperature can be used as a method of accelerating the rate of glass corrosion provided it can be shown that the reaction mechanism does not change over the range of temperatures studied.

In general, for any chemical reaction step, the temperature dependence can be quantitatively expressed through the Arrhenius equation:

$$k = A \exp\left(\frac{-E_{act}}{RT}\right) \tag{20}$$

where k is the reaction rate constant, A is a pre-exponential term, E_{act} is the activation energy, T is the absolute temperature, and R is the gas constant. The overall temperature dependence for glass dissolution depends on such factors as glass composition, solution composition, and the dominant reaction process.

The Arrhenius equation has been applied to the study of a number of individual glass reaction steps, including molecular water diffusion [SMETS-1984; TOMOZAWA-1989; MAZER-1991a; ZHANG-1991], ion exchange [WESTSIK-1980, -1981], and network dissolution [HENCH-1978]. Examples of dissolution data obtained from studies of the temperature dependence of HLW glass corrosion are presented in Fig. 2-23. In general, the temperature dependence of overall glass corrosion, as measured by the release of individual elements, is complex, suggesting that different reaction steps control the release of individual elements, and that the rate-controlling steps may also change with time and experimental conditions (see Section 1.0). However, the measured activation energies should indicate what types of reaction processes are important. The range of activation energies reported in the studies identified above are summarized in Fig. 2-24; for comparison, the experimentally determined activation energies for precipitation and etching/surface reactions of silicate minerals are also presented. Activation energies of approximately 70 to 320 kJ/mol are characteristic of silicate mineral bond-breaking processes [LASAGA-1981]. Activation energies for the formation of some of the secondary minerals known to occur on HLW glasses, such as clays and zeolites, typically range from 30 to 80 kJ/mol [MAZER-1991a].

The activation energies reported in the literature for the overall corrosion reaction for HLW glasses range from approximately 20 to 150 kJ/mol (Fig. 2-24). One review of the temperature dependence of waste glass reported that activation energies for corrosion between 25 and 300°C ranged from 70 to 144 kJ/mol [CHICK-1983]. Another review concluded that waste glass activation energies could be classified into two groups, one greater than 65 kJ/mol and one less than 30 kJ/mol [CONRADT-1985b]. The larger values were thought to be consistent with an ion-exchange and network-hydrolysis mechanism. Activation energies less than 30 kJ/mol were thought to reflect the presence of another, unidentified reaction process [CONRADT-1985b].

2.4.1 SRL 131 Glass

The temperature dependence of the reaction of SRL 131 glass and deionized water under leaching conditions and various flow rates between 23 and 120°C has been investigated with IAEA flow tests, as illustrated in Fig. 2-25 [BARKATT-1986]. Reaction progress was monitored by measuring the release of Si, B, Al, Na, Cs, and Sr to solution with time. Activation energies ranging from 100 ± 13 kJ/mol at high flow rates (250 m/yr) to 21 ± 2 kJ/mol at low flow rates (2 m/yr) were reported for tests that lasted up to 100 days [BARKATT-1986]. Significant changes in activation energy at different test conditions (i.e., flow rate) are consistent with a change in the rate-determining step of the overall reaction. The activation energies found for the weathering of SRL 131 glass (75 kJ/mol; see Section 3.4) are bracketed by these values [BATES-1982a, -1982b].

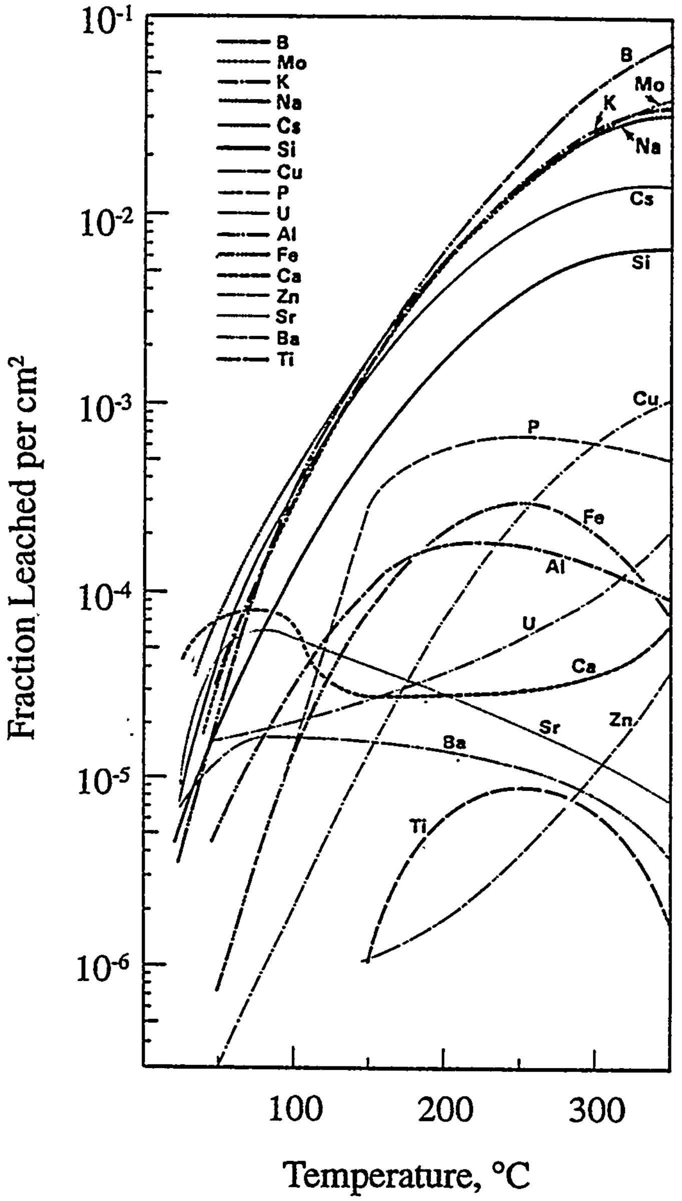

Fig. 2-23. Dissolution Data from Temperature Dependence Studies Used to Derive Activation Energies (adapted from [WESTSIK-1981]).

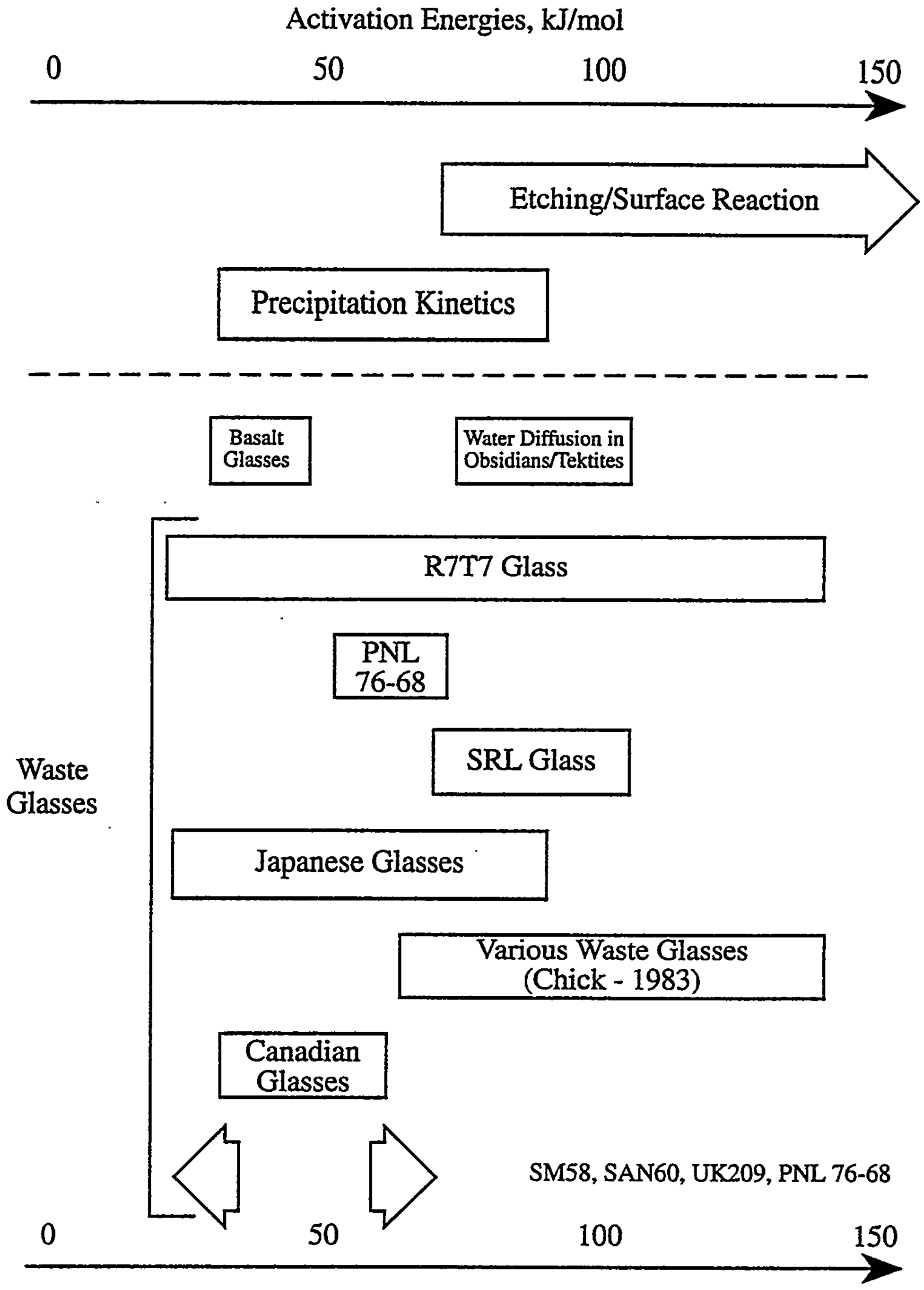

Fig. 2-24. Summary Diagram Indicating Reported Activation Energies for Individual Reaction Processes and Overall Activation Energies for HLW Glass Studies. The natural analogue studies (basalt glass, obsidians, and tektites) are discussed in Section 5; the HLW glass studies are discussed in Section 2.4.

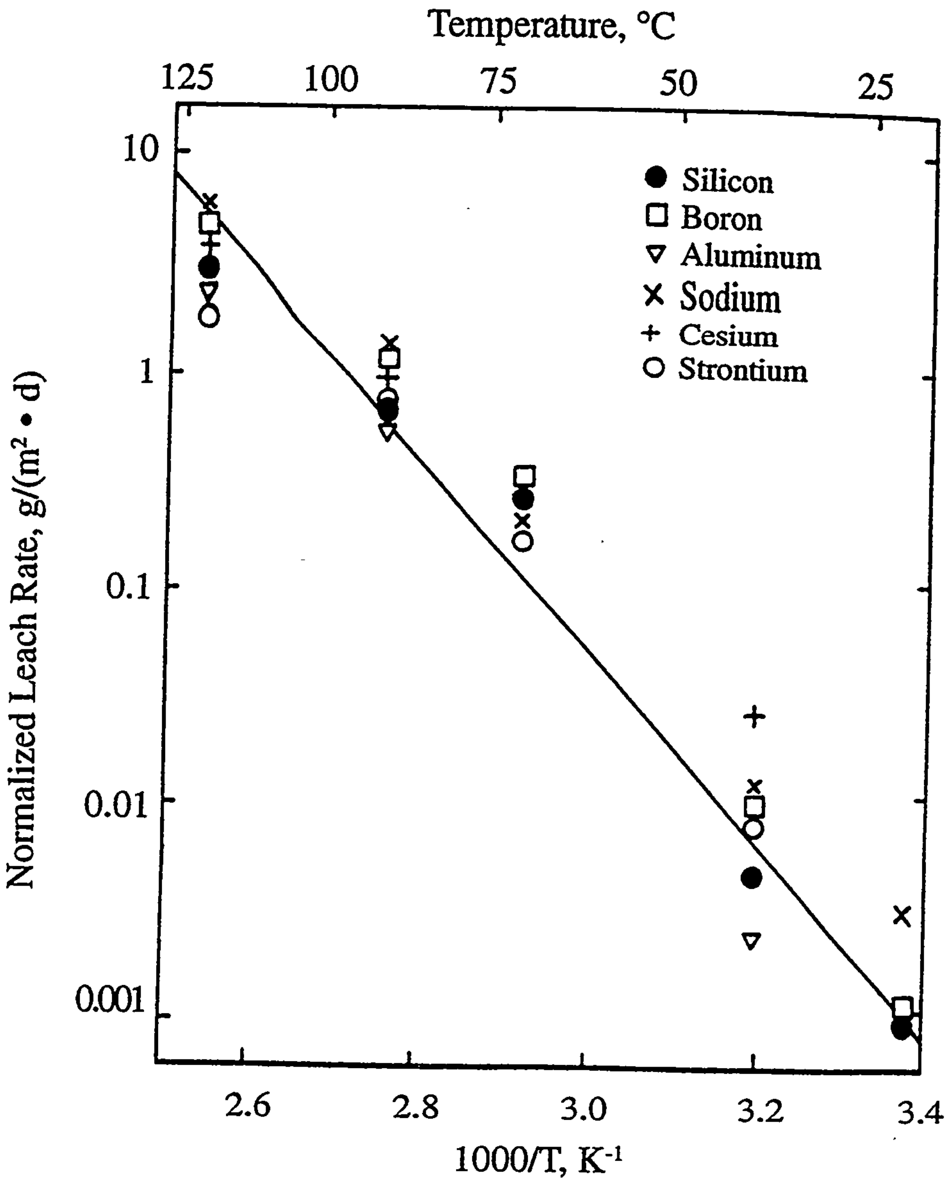

Fig. 2-25. Arrhenius Diagram of Leaching Data for SRL 131 Glass (adapted from [BARKATT-1986]).

2.4.2 R7T7 Glass

The temperature dependence for the reaction of R7T7 glass with distilled water between 100 and 250°C has been investigated in leach tests that lasted up to 28 days [VERNAZ-1988a]. Reaction progress was monitored by measuring the increase in concentration of Si and B in solution with time. Activation energies were found to range from 24 to 58 kJ/mol at temperatures up to 200°C and about 150 kJ/mol at temperatures above 250°C. The different activation energies were interpreted to be due to a temperature-induced change in the rate-controlling process of glass corrosion [VERNAZ-1988a].

A later study of the temperature dependence of R7T7 corrosion between 90 and 250°C examined the initial dissolution kinetics or forward reaction rate using a high-temperature Soxhlet device [DELAGE-1991]. The results are shown in Fig. 2-26. The activation energy was determined to be 59 kJ/mol, a value described as typical of surface reaction control [DELAGE-1991]. The activation energy of the long-term corrosion of R7T7 was measured to be 90 kJ/mol in leach tests with Mg- or Na-rich brines with powdered glass at 110, 150 and 190°C for up to 800 days at S/V ranging from 10 to 21,000 m^{-1} [GRAMBOW-1992a]. This 90 kJ/mol value was interpreted as resulting from water diffusion controlled by network hydrolysis. In temperature-dependence studies of short-term R7T7 glass dissolution below 250°C, the activation energy values were 60 kJ/mol, which is consistent with surface dissolution reaction control [DELAGE-1991; VERNAZ-1988a] and differs from the long-term temperature dependence of 90 kJ/mol [GRAMBOW-1992a].

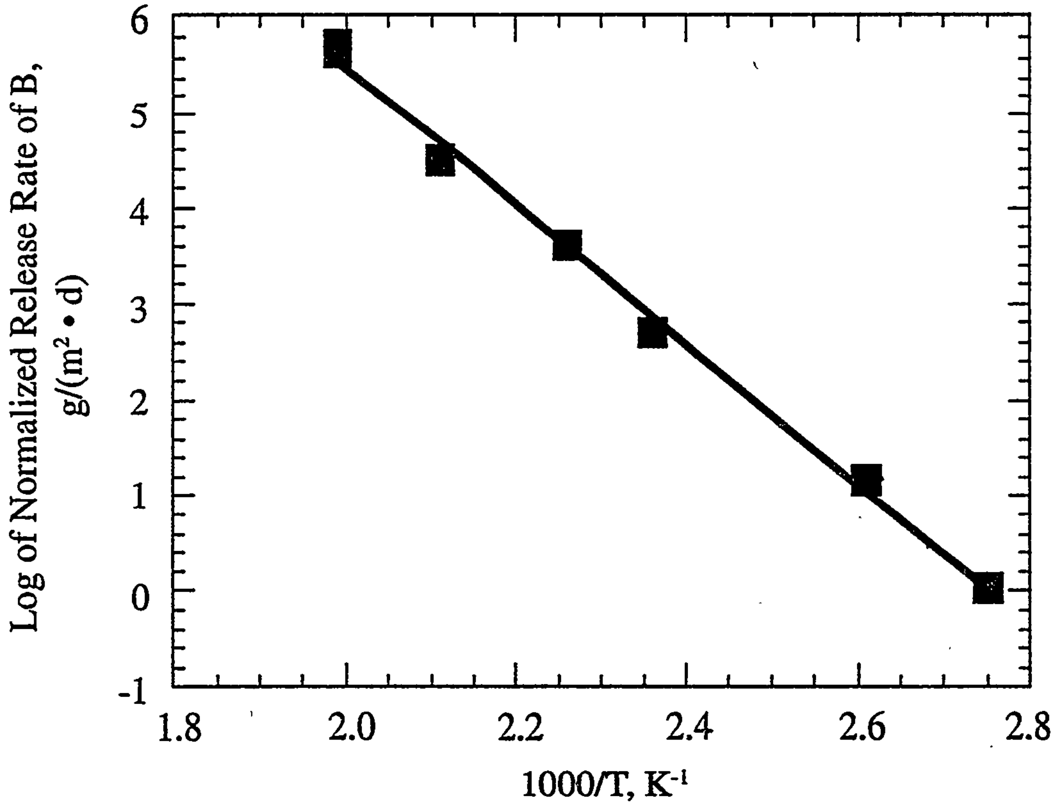

Fig. 2-26. Arrhenius Diagram of Leaching Data for R7T7 Glass in a Soxhlet Device (adapted from [DELAGE-1991]).

2.4.3 PNL 76-68 Glass

The activation energy for PNL 76-68 glass reacted with distilled water for up to 17 days between 4 and 90°C ranged from 50 to 67 kJ/mol, as shown in Fig. 2-27 [BARKATT-1981b]. Reaction progress was monitored by measuring the increase in concentration of Si, Na, Cs, Sr, Fe, and B with time. The rate-controlling process in these tests was thought to be a diffusion-controlled ion-exchange reaction [BARKATT-1981b]. The investigators noted that the observed overall activation energy was a composite term arising from diffusive ion exchange and matrix decomposition and dissolution. Another study of the temperature dependence of PNL 76-68 glass reacting with water was carried out between 25 and 350°C, as shown in Fig. 2-28 [WESTSIK-1981]. This study concluded that the glass/water reaction mechanism (mechanism unidentified) changed at 250°C; the activation energy below 250°C was reported as 53 kJ/mol. The nonlinearity at lower temperatures may suggest the mechanism may change near 100°C, as well.

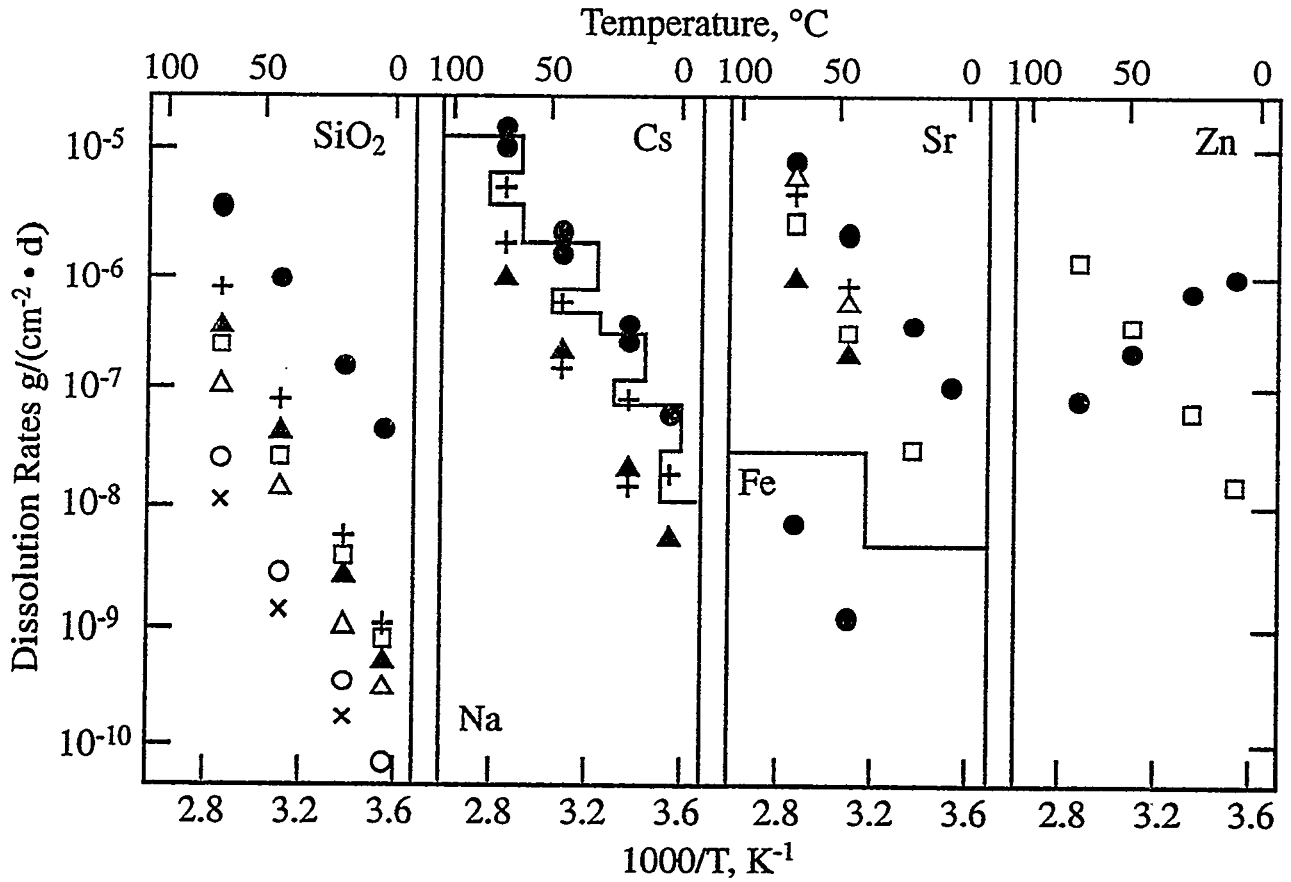

Fig. 2-27. Arrhenius Diagram of Leaching Data for PNL 76-68 Glass (filled circles) Reacted with Water at 4 to 90°C (adapted from [BARKATT-1981b]). Other symbols represent test results for other silicate glasses.

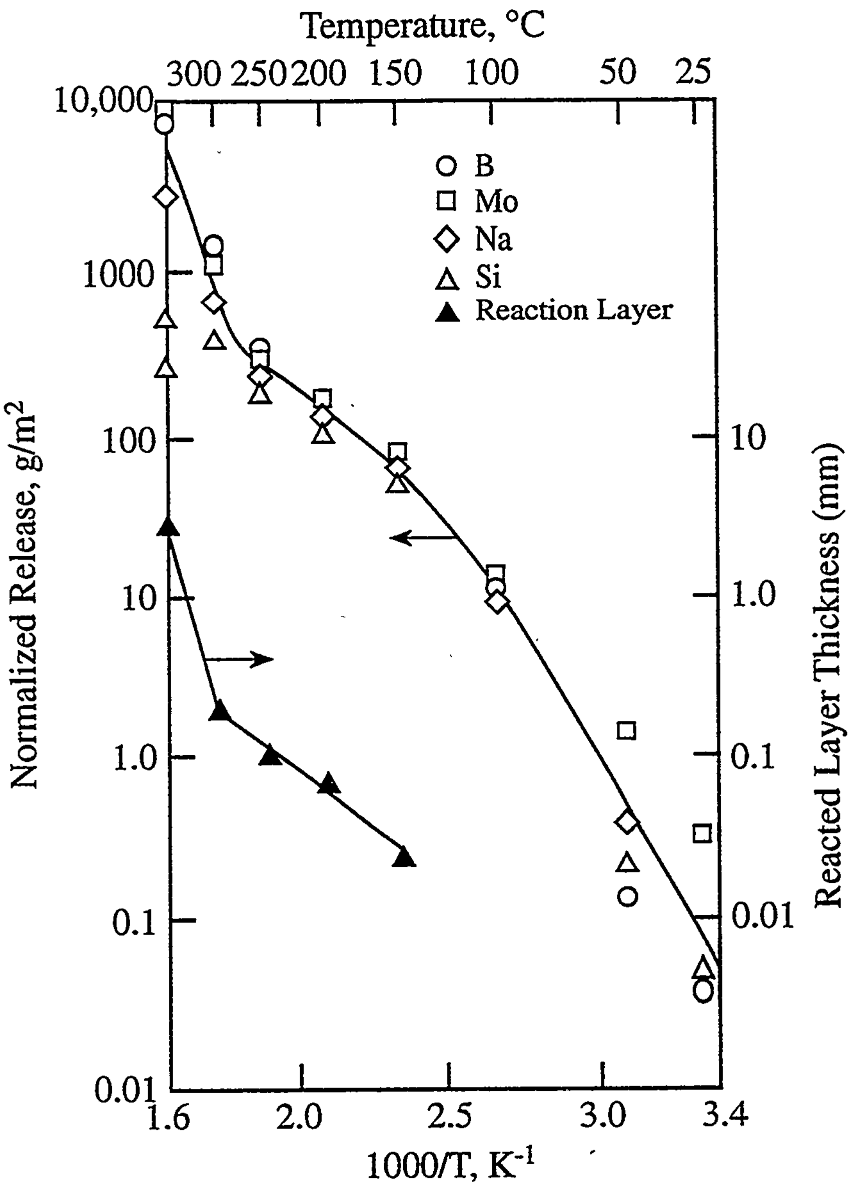

Fig. 2-28. Arrhenius Diagram of Leaching Data for PNL 76-68 Glass Reacted with Water at 25 to 350°C (adapted from [WESTSIK-1981]).

2.4.4 Japanese Waste Glass

The temperature dependence of the corrosion rate for a ^{238}Pu-doped Japanese waste glass was measured in leach tests with deionized water for up to 64 days between 23 and 70°C, as shown in Fig. 2-29 [BANBA-1989]. An activation energy of 80 ± 9 kJ/mol was determined on the basis of increased concentrations of Si, Na, Sr, and Cs in solution. The reaction mechanism responsible for the glass alteration was not identified. An activation energy of 22 ± 10 kJ/mol was determined based on Pu release from glass. This lower activation energy was attributed to the formation of a Pu-bearing mineral [BANBA-1989]. Thus, the change in concentration of Pu in solution was thought to be controlled by precipitation kinetics.

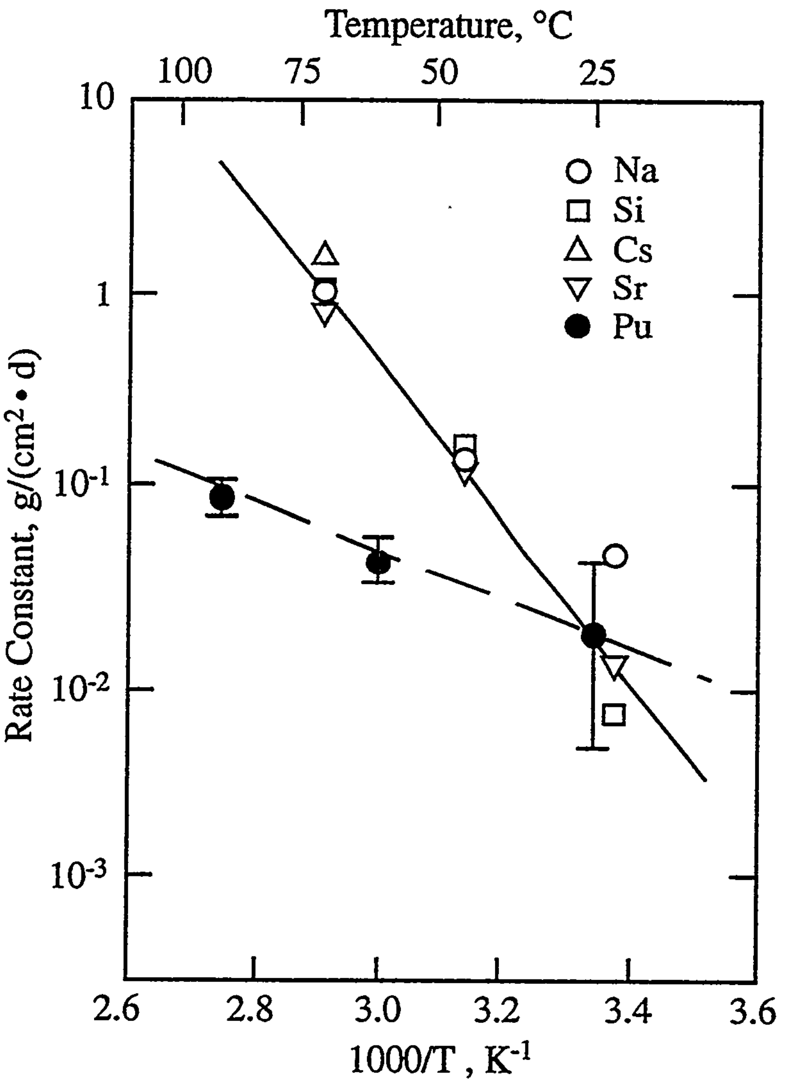

Fig. 2-29. Arrhenius Diagram of Leaching Data for ^{238}Pu-Doped Glass (adapted from [BANBA-1989]).

2.4.5 European Waste Glasses

Corrosion of several proposed European waste glasses (including SM58, SAN60, R7T7, SON58, and UK209) was studied in leach tests with distilled and clay waters for up to 30 days between 40 and 200°C, as shown in Fig. 2-30 [VAN ISEGHEM-1982]. This study concluded that no simple temperature dependence could be determined from the experimental results and the observed behavior might be due to a change in the corrosion mechanism resulting from changes in the reaction temperature [VAN ISEGHEM-1985].

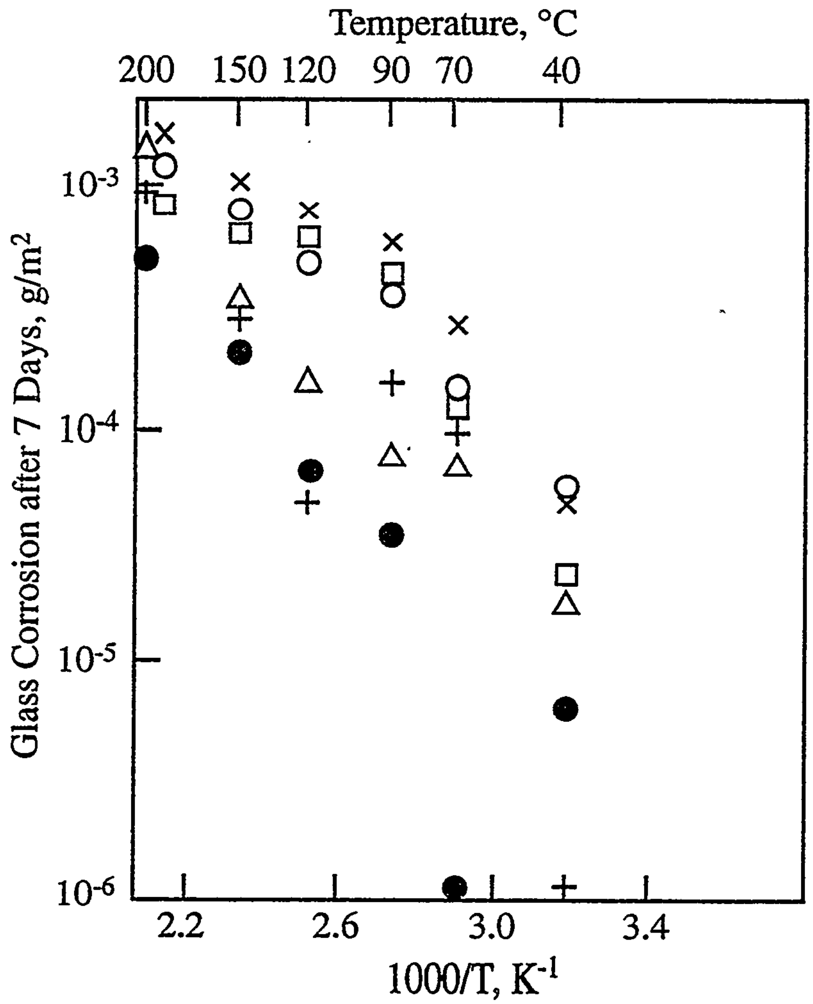

Fig. 2-30. Arrhenius Diagram of Leaching Data for Several European Waste Glasses (adapted from [VAN ISEGHEM-1982]). Open triangle = SAN60; X = SON58; open circle = SON64; filled circle = C31; open square = SM58; cross = UK209.

2.4.6 Canadian Waste Glasses

Alkali aluminosilicate Canadian waste glasses containing up to 20% simulated fission products were leached in static leach tests with deionized water between 25 and 99°C for up to 365 days [TAIT-1983]. Reaction progress was monitored by measuring the release of Si and Na to solution as a function of time; Na release was always greater than Si release. Apparent activation energies of 54 ± 8 kJ/mol for Si and 32 ± 4 kJ/mol for Na were measured for leaching times of 100 and 365 days. The lower value for Na release to solution was attributed to a diffusion-controlled leaching mechanism, whereas Si release was thought to be controlled by etching of the glass network [TAIT-1983].

2.4.7 Summary

- The dependence of waste glass corrosion rates on reaction temperature has been addressed in a number of experimental studies using the Arrhenius equation. The reported activation energies associated with the reaction of nuclear waste glass range from 22 to 150 kJ/mol.
- The range of observed activation energies is the result of the large range of variables studied including glass composition, evolving solution chemistry, reaction time, and temperature, in addition to the complex nature of glass corrosion mechanism.
- Activation energies have been attributed to various rate-controlling reaction steps, such as ion exchange, secondary phase formation, or surface reaction. They are not, however, diagnostic for identifying rate-determining steps in glass corrosion.
- For extrapolation of results to temperatures beyond the range covered by experimental measurements, it is necessary to establish that the rate-controlling step does not change with temperature. In several studies of the temperature dependence of waste glass reaction, it has been found that one or more activation energies can be derived for the temperature range examined.

2.5 Effects of Radionuclide Decay

Radiation effects on HLW glasses are an important consideration for radionuclide immobilization because of the potential to influence glass stability. Radiation can influence glass stability through formation of radiolytic products in the air and liquid water contacting the waste package, which may be more corrosive, or by physically altering the structure of the glass through atomic displacements.

Glass waste forms will exhibit temporal variations in both types and intensities of radioactivity. During the first 500 years of repository operation, when the radiation source would be most intense, radiation emissions are expected to be dominated by beta and gamma radiation from ^{137}Cs, ^{90}Sr, and other fission products (Table 2-6). Actinide elements that emit alpha particles (U, Np, Pu, Am, and Cm) generally have much longer half-lives (from hundreds to billions of years) and thus will become the dominant radiation source at longer times to the point where the alpha dose exceeds that from beta and gamma emissions. Because of their low penetrating ability in solids, alpha and beta particles can interact with the waste package environment only after the waste container has been breached and the air/water vapor environment of the repository comes in direct contact with the glass. Gamma radiation

Table 2-6. Cumulative Decay Events and Dose Projections for WVDP and SRL Glasses

Time (yr)	Alpha Decays (per cm^3)*	Beta Decays (per cm^3)*	Alpha Dose (rad)	Beta and Gamma (rad)
1	5×10^{14}	4×10^{17}	2×10^{7}	6×10^{8}
10	5×10^{15}	4×10^{18}	2×10^{8}	6×10^{9}
10^2	5×10^{16}	7×10^{18}	2×10^{9}	6×10^{10}
10^3	3×10^{17}	4×10^{19}	9×10^{9}	6×10^{10}
10^4	8×10^{17}	4×10^{19}	3×10^{10}	8×10^{10}
10^5	4×10^{18}	4×10^{19}	4×10^{10}	1×10^{11}
10^6	3×10^{18}	4×10^{19}	8×10^{10}	1×10^{11}

*Calculated from data in Weber [WEBER-1991], assuming a glass density of 2.7 g/cm^3.

can penetrate the waste canister walls and interact with the environment surrounding the waste package. However, because gamma-emitting sources have relatively short half-lives, their importance for radiolysis lessens as the waste glass becomes older [WEBER-1991]. A small portion of the radionuclides present in the glass may also undergo spontaneous fission, producing neutrons and two intermediate-sized fission atoms. Secondary (alpha, n) reactions may also contribute to neutron radiation from the waste. Although spontaneous fission and (alpha, n) reactions will be highly energetic sources of radiation damage, their overall contribution to the radiation effects are negligible because of their relatively infrequent occurrence [LUTZE-1988b, pp. 66-71].

2.5.1 Air and Water Radiolysis

Many studies have investigated the effects of radiation on glass leaching in air-water systems. Ionizing radiation will excite electrons and ionize water molecules and dissolved gases to form reactive radicals and new molecules [COHEN-1969; TAIT-1986; SUNDER-1992]. The predominant species formed (Table 2-7) include hydrogen ions (H^+), hydrated electrons (e^-_{aq}), hydrogen atoms (H•), hydroxyl (•OH), hydroperoxyl (HO_2•), molecular oxygen anions (O_2^-), molecular species hydrogen (H_2), and hydrogen peroxide (H_2O_2). The efficiency of radiation in producing radicals or molecules is expressed as a "G-value," which is the average number of radiolytic species created (positive G) or destroyed (negative G) by the absorption of 100 eV of radiation energy. A comparison of the G-values for radiolysis of water indicates that gamma radiation produces relatively greater concentrations of e^-_{aq}, H^+, •OH, and H•, whereas alpha yields are greatest for HO_2• , H_2, and H_2O_2 molecules (see Table 2-7) [MENDEL-1984].

Dissolved molecular nitrogen and carbon dioxide in the water may also undergo radiolytic decomposition that involves a several-step recombination of the dissociation products with O_2, water, and other associated radiolytic products to form nitrogen and carboxylic acids, respectively [BURNS-1982a, -1982b; BARKATT-1982, -1983a; MENDEL-1984; BIBLER-1987]. Because the solubility of N_2 in water is low, G-values for nitric acid production in air-saturated water will be small. The G(NO_3^-) values reported for irradiated oxidized water systems range from 0 to less

Table 2-7. Principal Radiolytic Species G-Values for Gamma and 5 MeV Alpha Radiation of Liquid Water [MENDEL-1984]

Species	H^+	e^-_{aq}	H•	•OH	HO_2•	H_2	H_2O_2	H_2O
Gamma	2.7	2.7	0.61	2.86	0.03	0.43	0.61	-4.14
Alpha	0.3	0.3	0.3	0.5	0.10	1.4	1.3	-3.3

than 0.2 [DOLLE-1978; RAI-1980a; RAE-1985; LINACRE-1981; GRAY-1984; REED-1990]. The G-values reported for radiolytic production of nitric acid from moist air or two-phase air/liquid water systems are about 2.0 from gamma, alpha, electron, and mixed neutron-gamma irradiation studies [PRIMAK-1955; JONES-1959; LINACRE-1981; REED-1987, -1990, -1991; WRONKIEWICZ-1991]. The irradiation of solutions containing organic compounds, such as methane, leads to the formation of methyl radicals that can combine to produce organic compounds of higher molecular weight that are similar to those of carboxylic acid radiolysis [MENDEL-1984]. Reed [REED-1991] also reported that small amounts of ammonia can be produced in irradiated air-water vapor and N_2-water vapor systems.

A notable decrease occurs in the pH of deionized water exposed to gamma and alpha radiation due to the formation of nitric acid in the irradiated air above the test solution and its subsequent dissolution in water [PRIMAK-1955; JONES-1959; LINACRE-1981; BURNS-1982a; NICOLOSI-1985; REED-1990, -1991; WRONKIEWICZ-1991]. Burns et al. [BURNS-1982a, -1982b] formulated an equation to predict the molar concentration of nitric acid accumulating in water by using the values determined for $G(NO_3^-)$, the concentration of N_2 in the atmosphere, the gas/liquid ratio, the dose rate, and the exposure time. These calculated pH values can then be used to predict the reaction behavior of glass samples in irradiated systems.

Radiolysis of water may also increase the redox potential (Eh) of the irradiated solution. During irradiation of water, equal amounts of reducing and oxidizing species are produced [MENDEL-1984; SUNDER-1992]. Hydrogen produced during both alpha and gamma radiolysis is chemically inert toward low-temperature (<100°C) aqueous reactions and has a high diffusional mobility relative to other radiolytic products. Thus, H_2 may separate from the aqueous system, resulting in an increase in the oxidizing conditions of the irradiated groundwater. Sunder and Shoesmith [SUNDER-1992] noted that with spent fuel radiolysis, O_2^- and •OH were the predominant oxidizing agents, followed by H_2O_2 and then O_2. Alpha and gamma radiolysis of brines has resulted in very high redox potentials due to scavenging of OH radicals by halide anions and a resultant increase in the separation of H_2 from the aqueous phase [GRAY-1985; JAIN-1985]. The presence of iron(II) and other reduced species may mitigate against oxidization of groundwaters [JANTZEN-1985c; GRAY-1988].

2.5.2 Solid Phase Damage

Radiation damage processes to HLW glass can be divided into displacement and ionization effects. The type of damage that occurs will depend upon the radiation interacting with the glass and the properties of the waste glass. A number of comprehensive reviews on solid radiation damage exist in the literature and are incorporated into the following discussion [WEBER-1983a, -1983b, -1984, -1988, -1991; BURNS-1982a; PRIMAK-1983; MENDEL-1984; DAY-1985; IAEA-1985; LUTZE-1988b; BIBLER-1988a; MATZKE-1988].

2.5.2.1 Displacement Damage

The volume (or density) of glass and crystalline materials may change as a result of atomic displacements that occur after exposure to radiation sources [MATZKE-1982; WEBER-1983a; IAEA-1985; MARPLES-1988]. For example, crystalline or ceramic waste forms may swell up to 10% after exposure to alpha radiation because of the increasing disorder of the crystalline material (Fig. 2-31) [McVAY-1981a; WEBER-1982, -1984]. Volume changes in glass after alpha exposure are generally ±1.2%. Exarhos has noted that displacement damage causes marked swelling and eventual amorphization in crystalline materials, while ionization damage causes only slight swelling with no tendency towards amorphization [EXARHOS-1984a]. Measurable volume changes for glass first occur after a cumulative exposure of 1 x 10^{17} alpha decays/cm^3, and reach a maximum after a dose of 5 x 10^{18} alpha decays/cm^3 [WEBER-1984]. A comparison of these damage and saturation levels with the expected cumulative alpha exposure levels for WVDP and DWPF glasses indicates that waste form volume changes may occur after about 1000 years of self-irradiation damage, provided that annealing processes do not erase the damage (see Table 2-6) [WEBER-1983a, -1983b, -1988; MENDEL-1984].

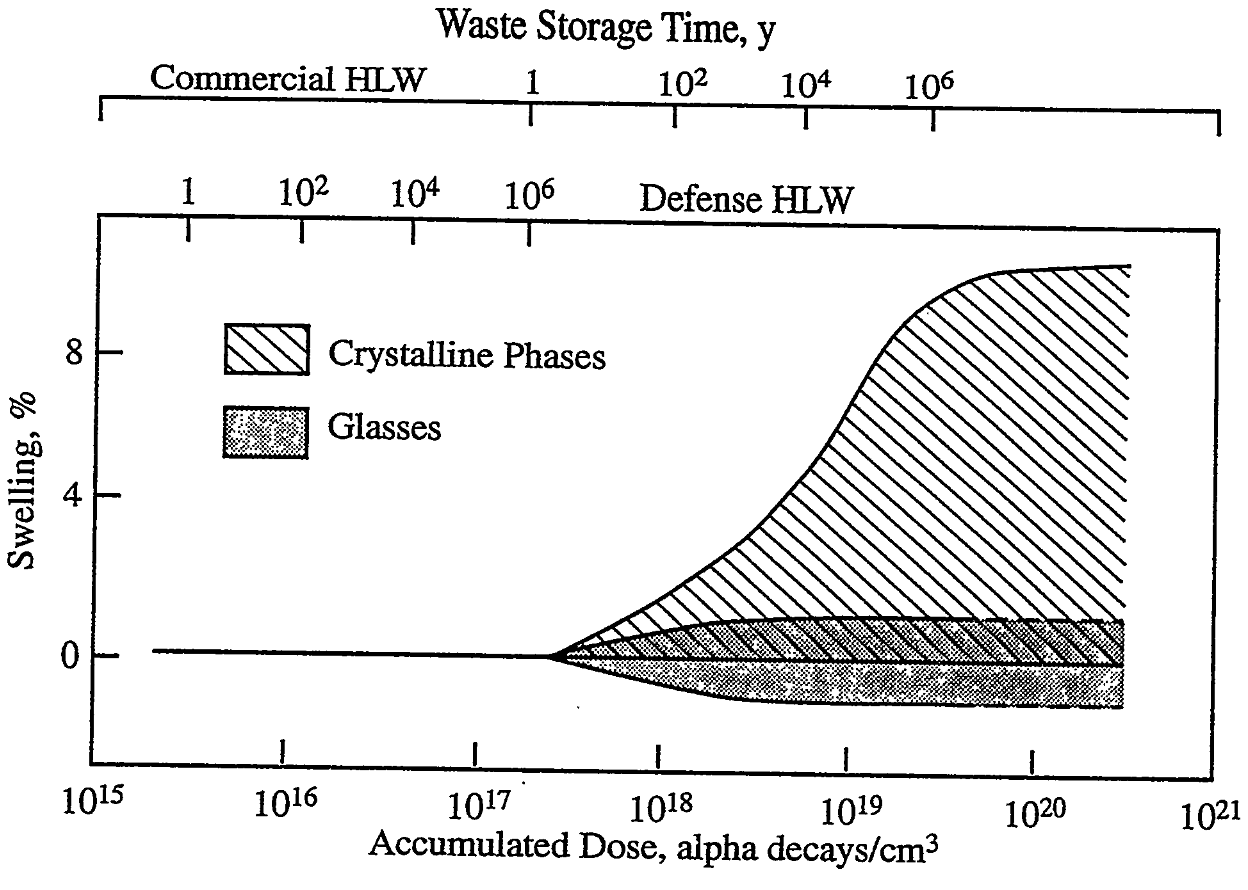

Fig: 2-31. Range of Swelling in Volume Percent for Crystalline and Glass Waste Forms as a Function of Accumulated Dose (and Repository Storage Time) (adapted from [McVAY-1981a]).

Radiation damage from alpha decay results from interaction of the glass with both a high-energy alpha particle (about 4 to 6 MeV) and a lower energy alpha-recoil nucleus (about 0.1 MeV). Because an alpha particle has an appreciable mass, its ejection will impart recoil energy to the alpha-recoil decay product. The alpha-recoil nucleus will transfer this energy as it collides with surrounding atoms, displacing several thousand atoms along an alpha-recoil track in the surrounding glass [WEBER-1983a, -1983b]. The emitted alpha particle dissipates most of its energy in the surrounding medium by an ionization process, but near the end of its track produces enough low-velocity collision events to displace several hundred atoms. Alpha particle damage tracks in glass are about 10,000 nm long, whereas alpha-recoil damage tracks are about 10 nm long [EWING-1990]. Beta radiation is expected to result in less than one direct displacement per decay event, and direct displacement from gamma radiolysis is negligible.

Solid-phase radiation-damage studies have focused on alpha particle and alpha-recoil damage effects because of the relatively short half-lives of the beta and gamma radiation sources. Alpha-doping simulation experiments thus emphasize displacements from alpha decay events but do not account for the high ionizing doses of beta and gamma radiation to which the actual waste glass will initially be exposed. The ionizing dose received by the waste from alpha particle sources is also significant, with cumulative dose exposures from alpha sources expected to exceed those from beta-gamma sources after about 10^6 years (see Table 2-6) [WEBER-1991]. Synergistic effects between alpha-collision and ionization processes may occur in actual vitrified wastes, but such effects are generally not simulated in short-term radiation experiments [ROBERTS-1981].

Primak [PRIMAK-1983] and Arnold [ARNOLD-1985, -1988] subjected vitreous silica and borosilicate glasses to He-, Xe-, and Pb-ion bombardment to simulate the effects of alpha-particle damage to glass. Three interactive processes are believed to cause the alternate swelling and shrinking that was noted in the glasses during irradiation. An initial expansion of 0.1% was associated with the formation of defect centers and valence changes. This expansion was followed by a contraction of 0.1% associated with the dissipation of particulate radiation and a second phase of 1% contraction associated with the intense excitation found in the last fraction of the energy range of a heavy atom [PRIMAK-1983]. Primak noted that the initial expansion occurred rapidly, saturated, and eventually was overtaken by the ongoing contraction. Borosilicate and complex HLW glasses display ion bombardment stresses that correlate with ionization processes, whereas fused silica samples have stresses associated with displacement damage [ARNOLD-1985, -1988].

Glass samples irradiated by neutrons that produce $^{10}B(n, alpha)^7Li$ reactions expanded within the range of 0.12 to 0.6%. Sato et al. [SATO-1984, -1988, -1989, -1990] attributed this glass swelling to the formation of He bubbles that became entrapped within damaged zones of the glass. When at rest, the alpha particles emitted during actinide decay fill their valence-electron vacancies to become He atoms. Similar He-filled microvoids have been observed in naturally occurring metal oxide phases, with the accumulation of He resulting from either slow diffusion of He through the solids or exclusion of He from the mineral structure [HEADLEY-1981]. Matzke [MATZKE-1982] suggested that bubbles in irradiated nonfissile materials form due to a coalescence of radiation-induced thermal vacancies and the driving force is the surface tension between the gas and the walls of the bubble.

Susman et al. [SUSMAN-1990] noted that an average total volume contraction of about 3% produced during neutron bombardment of vitreous silica actually relates to a contraction of 20% in the damage tracks, which are then left surrounded by undamaged material. To investigate this damage behavior further, the authors subjected vitreous silica samples to pressures of 16 GPa in a diamond anvil cell; the resultant damage was related to extensive intermediate-range disorder, although some short-range silicate tetrahedron deformation was also identified. Primak [PRIMAK-1983] attributed the silicate tetrahedron deformation to a decrease in the silicon-oxygen bond angle, resulting in a rapidly "quenched" compacted structure.

A significant proportion of crystalline material contained within the glass may be detrimental to waste form integrity because of differences in the radiation-induced volume expansion of glass vs. crystalline waste products (Fig. 2-31). After radiation-induced amorphization, the more highly ordered crystalline materials show a greater amount of swelling than the less structured vitrified materials. Differential expansion of crystalline material and glass may result in fracturing and an increase in the surface area of the glass. Weber and Roberts [WEBER-1983a] reported microfracturing in ^{244}Cm-doped samples as a result of differential expansion associated with amorphization of crystalline phases after a cumulative exposure of 8×10^{17} alpha decays/cm^3.

Transmutation of fission products results in changes of both valence and ionic size of the daughter atom relative to its parent radionuclide. Most radionuclide transmutations are unlikely to directly affect the behavior of waste glass due to the wide range of elements acceptable in the glass matrix. However, transmutations that produce decay product nuclei that are insoluble in the glass may result in the nucleation of crystalline material [GRAY-1982; WEBER-1984]. Nucleation of crystalline phases, combined with the differential volume expansions exhibited by radiation-damaged glass and crystalline solids, could eventually contribute to fracturing of the waste form [WEBER-1983a, -1983b]. This fracturing process can increase the surface area of the glass.

With HLW glass, the beta-decay transmutations that occur most often, and their associated half-lives are as follows:

(1) $^{137}\text{Cs} \rightarrow {}^{137m}\text{Ba} + \beta^- \rightarrow {}^{137}\text{Ba}$ ($T_{1/2} = 30.2$ years) and

(2) $^{90}\text{Sr} \rightarrow {}^{90}\text{Y} + \beta^- \rightarrow {}^{90}\text{Zr}$ ($T_{1/2} = 28.8$ years) + β^-.

The transmutation of Cs to Ba should not alter the waste glass characteristics because both of these elements occupy similar structural sites as network-modifying atoms in the bulk glass [MEANS-1987]. The transmutation of Sr to Zr involves a change from a parent nuclide that is a network modifier to a decay product that may be a network former. If the production of additional Zr by transmutation results in a total ZrO_2 concentration of about 2.3 wt.%, then the glass may become saturated with respect to Zr and crystalline phases will begin to nucleate [MEANS-1987].

Although DWPF glasses will contain combined ZrO_2 + SrO concentrations of <2.3 wt.%, other waste glasses, most notably the West Valley WV205 and the French R7T7 compositions, contain >2.3 wt.% ZrO_2 + SrO (see Volume I, Appendix A). Sufficiently large solid state diffusion rates and agglomeration of the radiogenetically produced "excess" Zr will also be required before significant crystal phase development can occur. Given the previous considerations of low ZrO_2 + SrO waste loadings and solid state diffusion requirements for Zr, it is considered unlikely that significant crystal phase formation will occur as a result of radionuclide transmutations in DWPF waste glasses.

An increase in fracture toughness, or resistance to fracture propagation as measured with various indentation techniques, has been reported for glasses exposed to various radiation sources. Increases up to 80% have been reported for glasses exposed to cumulative alpha exposures of 10^{18} to 10^{19} decays/cm^3 [ROUTBORT-1983; MATZKE-1988; -1989; WEBER-1988; VERNAZ-1991b], and increases were also observed for radiation damage from most ion beams [MATZKE-1984]. Increases in fracture toughness of highly damaged crystalline materials have been attributed to a more ductile behavior of the solids with increasing disorder and the arresting of tensional fracture growth in regions with residual compressive stresses, such as those that may exist around individual alpha-recoil tracks [CHAKOUMAKOS-1991]. Increased fracture toughness may provide an enhanced resistance to fracture propagation in vitrified waste. Ewing and Lutze [EWING-1990] attributed the increased fracture toughness in radiation-damaged crystalline phases to crack bowing, crack deflection, internal stresses associated with the coherency of secondary phases, and differences in elastic properties of phases at different stages of the damage process. Clinard et al. [CLINARD-1985] also indicated possible impedance of crack propagation by interaction with voids.

Displaced atoms that have a higher energy level than those in equilibrium positions may release their latent energy as heat when the waste form is thermally annealed [WEBER-1983a, -1983b]. A slow release of latent energy may be beneficial in leading to additional glass annealing because defect centers may be thermally unstable and will, therefore, anneal as the temperature is raised slightly [MATZKE-1982; PRIMAK-1983]. A compilation of saturated latent energy values in waste glass indicates a range of 50 to 125 J/g. An instantaneous release of this energy would result in a self-sustaining temperature rise of <130°C in the waste [WEBER-1983a, -1983b]. Generally, however, the stored energy is released over a broad temperature range, and the total energy released as a result of annealing decreases as the temperature of the waste form rises [ROBERTS-1976; MALOW-1982; IAEA-1985]. A single study that suggests latent saturation energy levels up to 400 J/g has been cited by Weber and Roberts [WEBER-1983a]. An instantaneous energy release of this magnitude would result in a temperature rise of the waste form of up to 400°C; however, such an extreme release of energy is unlikely in light of previously described results.

2.5.2.2 Ionization Damage

Glass ionization damage results from the excitation and ejection of electrons from the valence orbitals of the target atom by incident radiation. Although ionizing radiation produces few direct displacements, electron excitations, if they are localized and persistent, may eventually lead to atomic displacements [WEBER-1983a]. This ionizing damage may manifest itself in several forms, including electron hole pairs, covalent bond ruptures, valence changes, structural water decomposition, and decomposition of unstable molecular ions [WEBER-1983a, -1983b; EXARHOS-1984b; MEANS-1987].

The largest volume changes associated with gamma irradiation have been reported by Shelby [SHELBY-1980a], who noted a maximum compaction of about 1% for silica and borosilicate glasses. Sato et al. [SATO-1984] determined maximum swellings of 0.2 and 0.04% for borosilicate glass exposed to cumulative external gamma doses of 1×10^9 and 5×10^8 rad, respectively, and densification of 0.03 to 0.05% for high silica glass at 1.2×10^9 rad. Bibler [BIBLER-1982a] noted a density change of <0.05% for borosilicate glass exposed to cumulative doses of 8.5×10^{10} rad. Howitt et al. [HOWITT-1991] found a threshold dose for gamma irradiation damage of soda-silicate glass at about 10^8 rad and a saturation dose of about 10^9 rad. Comparisons of these data with combined beta and gamma doses expected for the HLW glasses suggest that these levels of radiation exposure may be readily attainable within the first 10 years after glass fabrication (Table 2-6).

The amount of structural damage incurred by a glass may also depend on the glass composition. The addition of B, an increase in the alkali/Si ratio, and an increase in compositional complexity have all been observed to enhance the rate of densification in gamma- and electron-irradiated glasses [SHELBY-1980a; PRIMAK-1983; SATO-1987; BIBLER-1988a; WEBER-1991], whereas glass samples with implanted hydrogen have expanded during irradiation [SHELBY-1979]. Several studies noted a suppression of the amount of radiation-induced damage, coloration, and leaching as a function of increasing Al, Ce, and water content [WEEKS-1964; FAILE-1970; DISALVO-1972; FRIEBELE-1978; MALOW-1980a; ACOCELLA-1982]. For example, the bridging oxygen between Al and Si may trap a hole during irradiation, allowing local charge-compensating alkalis to trap electrons and diffuse away [GRISCOM-1971]. The resultant hole-trapping by the bridging oxygen results in a 50% increase in Al-O bond lengths, thereby offsetting the intensity of the compaction process noted previously for displacement damage in some glasses.

Ruller and Friebele [RULLER-1991] suggested that when natural and synthetic high-silica glasses containing more than 150 ppm OH are irradiated, the radiolytic electrons and holes are trapped by the Si-OH, forming atomic hydrogen and NBO hole centers. The H_2 gas that subsequently forms may undergo a second reaction with the silica network, breaking the Si-O-Si bonds to produce SiOH and SiH groups that inhibit densification of the glass [SHELBY-1979]. This radiolytic disruption of the Si-O-Si bonds is also analogous to the network-hydrolysis process that results in corrosion of the glass.

Damage from gamma irradiation may manifest itself in bubble formation and phase separation after a threshold dose of about 10^8 rad and a saturation dose of about 10^9 rad for a variety of different glass compositions (Fig. 2-32) [DENATALE-1985; WEBER-1988; HOWITT-1991]. Bubble formation and phase separation have also been observed for glasses irradiated with electrons [MANARA-1982; DENATALE-1982a, -1982b, -1984; SATO-1983]. The mechanism of this bubble formation involves the disruption of nonbridging ionic bonds and electron capture by migrating cations such as Na^+ under an electric field generated across the glass [DENATALE-1984; HOWITT-1991]. Continued ionization of the glass in the absence of Na^+ leads to the formation of Si-O-Si bonds, O_2, and e^-, with the O_2 gas accumulating as bubbles within the glass. The formation rate of bubbles can be correlated directly with the Na_2O content of the glass; it is most pronounced under the influence of gamma irradiation, followed by ion irradiation, and then electron irradiation [MANARA-1984b; DENATALE-1984]. The G-value for the formation of O_2 in gamma-irradiated glass is about 0.1 [DENATALE-1985]. Heuer et al. [HEUER-1986] have confirmed the presence of generated gas in the bubbles by trapping gases escaping from irradiated glass with a carbon coating. These authors also noted that O_2 may recombine with waste components in the glass to form phases rich in waste elements but depleted in Si. Radiation-enhanced sodium mobility and subsequent bubble formation may occur during irradiation with an electron beam. Since these phenomena are not observed in glasses containing short-lived radionuclides, they are not likely to occur in waste glasses under actual disposal conditions [MATZKE-1992].

Tosten [TOSTEN-1989] irradiated glasses identical in composition to those of Howitt et al. [HOWITT-1991] at doses of up to 3.6×10^{10} rad and noted no associated bubble formation; he suggested that Howitt et al. may have induced bubble formation during their ion-milling sample preparation process. Similarly, Bibler et al. [BIBLER-1990a] gamma-irradiated borosilicate glass up to a cumulative dose of 3.1×10^{10} rad with no bubble formation; they also noted that bubble formation could be induced by the electron beam from the microscope.

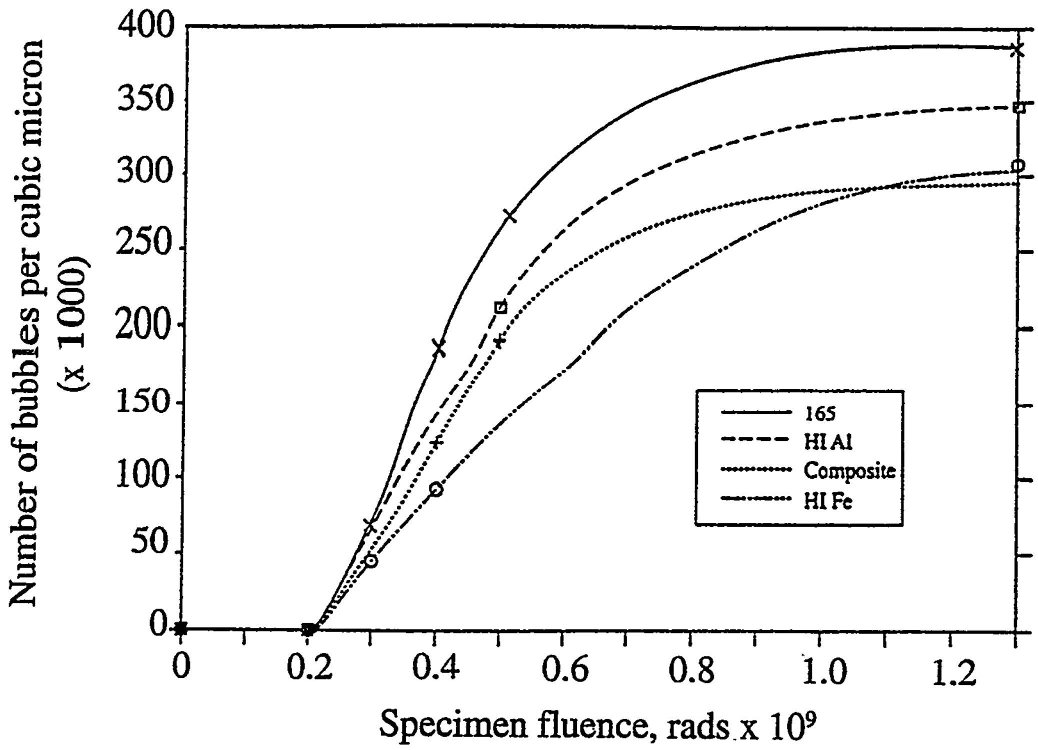

Fig. 2-32. Concentration of Oxygen Bubbles Produced in SRL Na-Borosilicate Glasses as a Function of Cumulative Gamma Dose. Dose rate to samples was 2.5 x 10^6 rad/h (adapted from [HOWITT-1991]).

Sato et al. [SATO-1984] observed 0_2 bubble formation during electron beam irradiation and a concurrent increase in volume of simulated waste glasses under a variety of radiation sources. In contrast to the studies of Howitt et al. [HOWITT-1991] and DeNatale and Howitt [DENATALE-1985], Sato et al. found swelling to be most pronounced under electron irradiation. When samples were exposed to an electron fluence of 2 x 10^{21} to 3 x 10^{22} e^-/cm^2, the simulated waste glasses swelled by about 50%. Swelling of this magnitude during electron irradiation can be correlated to the density of bubble formation within the glass, which, in turn, is dependent on the irradiation temperature and glass composition [MANARA-1984b].

2.5.2.3 Annealing Processes

The accumulation of radiation damage in glass is inversely dependent on the ability of glass to repair or anneal the radiation-damaged regions. A large increase in corrosion rates resulting from solid radiation damage will occur only if damage zones overlap to provide interconnected channelways between the interior of the sample and the surface. If individual damage zones anneal in relatively short times, it is plausible that the overlap of damage zones will not occur and significant increases in corrosion rates will not be realized. Most laboratory experiments accelerate glass reaction by increasing dose rates several orders of magnitude above levels that are pertinent to an actual waste glass. If the radiation exposure accelerates damage overlap relative to the annealing process, then an artificially accelerated corrosion rate may result.

Weber [WEBER-1988] has summarized experimental dose-rate and cumulative dose conditions under which ionization-induced glass decomposition has been observed (Table 2-8). Weber concludes that a dose-rate effect may exist for ionization-induced decomposition, so glasses irradiated at high dose rates may not accurately reflect the behavior of actual waste glasses at comparable doses.

The process of annealing has been addressed in numerous studies with crystalline materials [LUMPKIN-1988; EWING-1988; OLANDER-1989; WEBER-1990], but in relatively few studies with glass. The retention of alpha-decay damage in crystalline solids depends on the energy barrier of the solid to recrystallization. If the barrier is low enough, the radiation damage will anneal as it occurs. For alpha-damaged waste glass, Sato et al. [SATO-1989] have determined isochronal annealing changes as a function of temperature and isothermal annealing changes as a function of time. These results indicate that annealing processes readily diminish glass expansion damage within days after heating to 400 to 450°C, with slower recovery rates indicated at lower temperatures (Fig. 2-33). Burns et al. [BURNS-1982b] estimated a mean recovery time for damage tracks in glass of about three hours to 110 days (at 200 to 25°C, respectively). With critical damage zone overlaps occurring for alpha-simulated tests after about 1200 days, these recovery rates suggest that solid damage alpha-recoil tracks in the glass will readily anneal in the vitrified waste and, therefore, will not significantly affect the stability of the waste form.

Mark and Ritter [MARK-1987] and Walder and Märk [WALDER-1988] studied the annealing process in Na-silicate glass after inducing damage by fission products, alpha decays, and electron beams. These authors noted an Arrhenius temperature dependence of annealing rates that was generally independent of the source of radiation damage. Based on these relationships and the relatively low dose rates expected for vitrified nuclear waste, damage to the glass would be expected to anneal out as fast as it occurs, and there would therefore be little buildup. Marples [MARPLES-1988], however, indicated that, at 130 to 300°C, glass densities only followed an exponential annealing curve for a short time, with ~20 to 70% residual density change remaining even after long annealing periods. This residual damage would not be expected to significantly affect glass properties due to the relatively small density changes expected for radiation damage in the glass (see Fig. 2-31). Marples also notes that in tests with actinide-doped glass there may be some partial annealing of damage during testing, while at high dose rates characteristic of ion bombardment experiments, there will be almost none.

Table 2-8. Dose and Dose-Rate Dependence of Ionization-Induced Decomposition of Simulated Waste Glasses. After Weber [WEBER-1988].

Irradiation Method	Dose Rate (rad/h)	Cumulative Dose (rad)
Gamma	10^6 - 10^7	10^8 - 10^9
Ion	10^{10} - 10^{11}	10^9 - 10^{12}
Electron	10^{13} - 10^{15}	10^{13} - 10^{15}

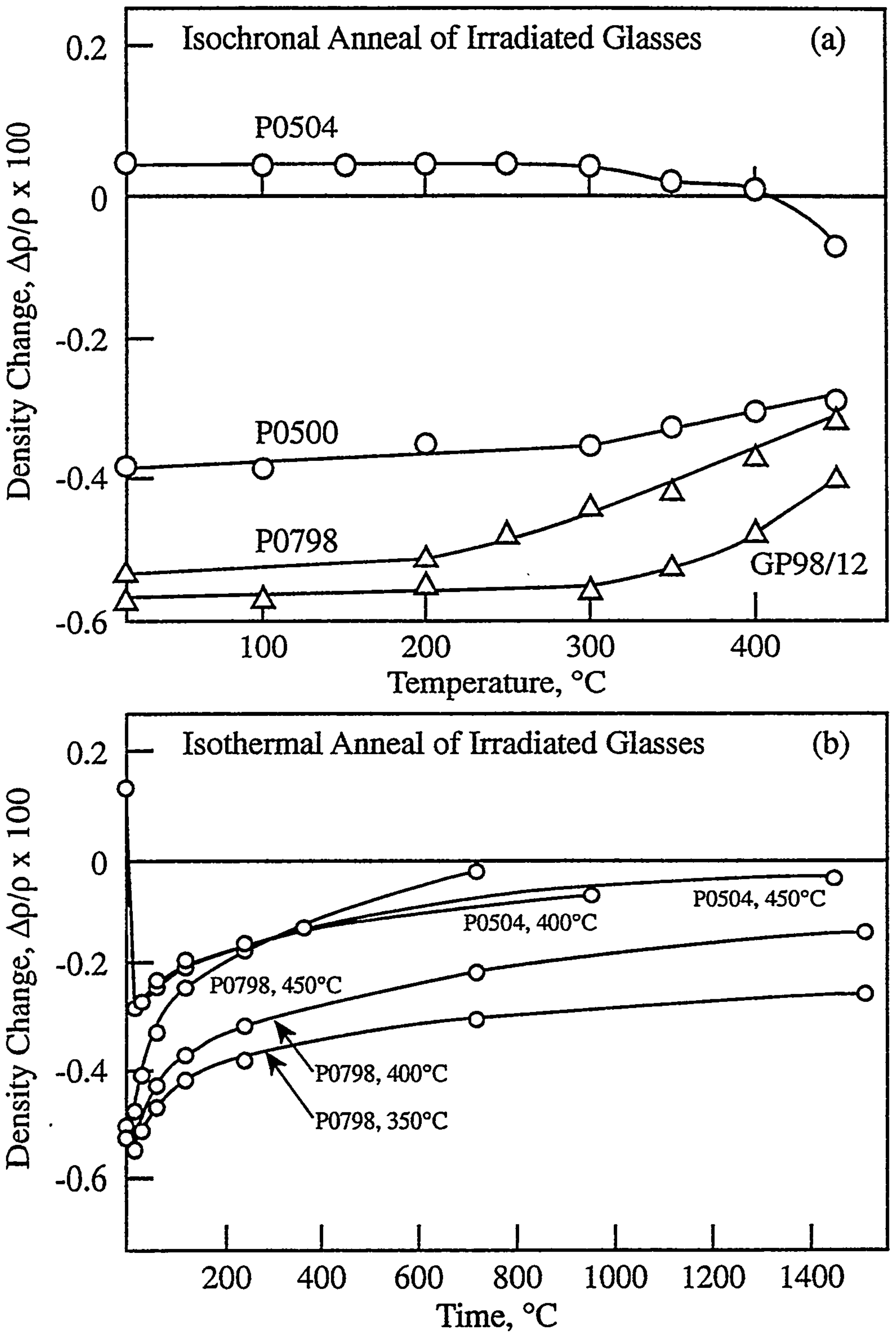

Fig. 2-33. Thermal Annealing Trends for (n, alpha) Irradiation in Four Types of Simulated Borosilicate Waste Glasses. (a) isochronal annealing changes as a function of temperature, (b) isothermal annealing changes as a function of time (adapted from [SATO-1989]). Glass compositions for "PO" prefix glasses given in Sato et al. [SATO-1988].

2.5.3 Effects on Glass Durability and Radionuclide Release

Evaluations of the radiolytic effects on glass reactions are quite complex due to interactions between the dissolving glass components, radiolytic products, and buffering capacity of silicate groundwater against radiolytically produced acids. Changes in microstructure and bonding have the potential to affect the integrity of waste glasses and their ability to retain radionuclides. Alpha tracks, phase changes, bubble formation, phase separation, and associated microfracturing [LUMPKIN-1988; EYAL-1990; WEBER-1991] also could increase the alteration rate of glass and crystalline solids by providing access channels for water entry, thereby increasing the surface area. The influence of annealing processes in limiting the cumulative radiation damage to solids also complicates interpretations of solid damage effects on glass alteration properties.

In experiments conducted with glass samples immersed in deaerated and deionized water at 50 to 90°C at 20 m^{-1}, the irradiated leachates displayed a larger increase in pH relative to their nonirradiated analogs (Fig. 2-34) [McVAY-1981b]. The higher pH values of the irradiated leachate solutions indicate a greater extent of glass reaction due to release of hydroxide from the altering glass. Furthermore, the difference in pH values between the irradiated and nonirradiated tests was lowest at the highest temperature of 90°C, indicating that the effects of radiolysis on the corrosion rate become less important at higher temperatures.

With tests in deaerated and deionized water at 20 m^{-1} [PEDERSON-1983c] and deaerated brines at 10, 100, and 1000 m^{-1} [PEDERSON-1984], the effects of gamma radiation on release rates of Na, Si, and B from PNL 76-68 glass progressively diminished as the reaction temperature increased from 50 to 90°C (Fig. 2-35). McVay et al. [McVAY-1981a] also note that release rates exhibited a dose rate dependence, with a 20% increase in Si release at 70°C and 10 m^{-1} resulting from a two-hundred fold increase in the dose rate.

In tests conducted with gamma-irradiated borosilicate waste glass in aerated and deionized water systems, dissolution rates of B, Al, Si, alkalis, and actinides from the glass generally increased three to five fold over nonirradiated tests but for individual elements varied less than 1 to 12 fold [McVAY-1980b, -1981a, -1981b; BARKATT-1982, -1983a; NASH-1982, -1983; PEDERSON-1983c]. Both the formation of nitric acid in the irradiated air above the aqueous solution and the formation of water dissociation products appear to have combined to accelerate glass reaction rates in these tests.

McVay et al. [McVAY-1981a] sequentially irradiated PNL 76-68 glass samples in the presence of air + water and deaerated water, or preirradiated solid glass samples prior to immersion in water at 10 m^{-1}. In these tests, the largest release rate increases for alkalis, Si, and B were recorded for samples irradiated in the presence of air + water, with slightly larger increases at 90°C than at 50°C. This temperature-dependent trend was opposite to that exhibited by samples irradiated in deaerated deionized water [PEDERSON-1981]. Irradiation in the deaerated water systems accelerated glass reaction rates up to about 60% of the level that characterized the aerated samples, indicating that nitric acid and water radiolytic products were equally responsible for the enhanced corrosion observed in the aerated tests. Glass samples that were irradiated prior to being immersed in deionized water did not display any increase in release rates. Comparative MCC-1 tests between gamma-irradiated brines and deionized water indicate that dissolution rates of Si are three or four times lower in brine [BIBLER-1982a].

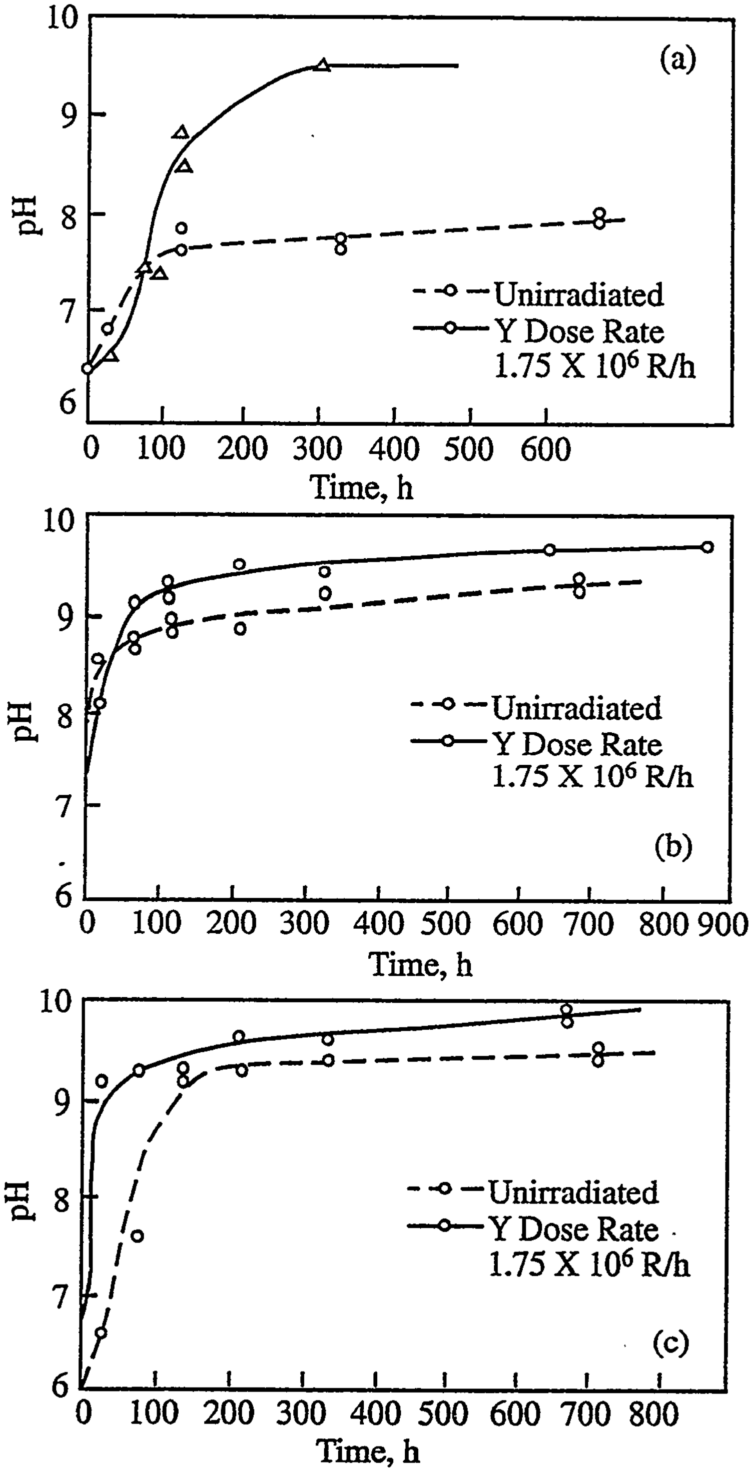

Fig. 2-34. Deionized and Deaerated Leachant pH Trends for Gamma-Irradiated vs. Nonirradiated Static Leach Tests (S/V = 20 m^{-1}) with PNL 76-78 Glass. (a) 50°C trends, (b) 70°C trends, and (c) 90°C trends (adapted from [McVAY-1981b]).

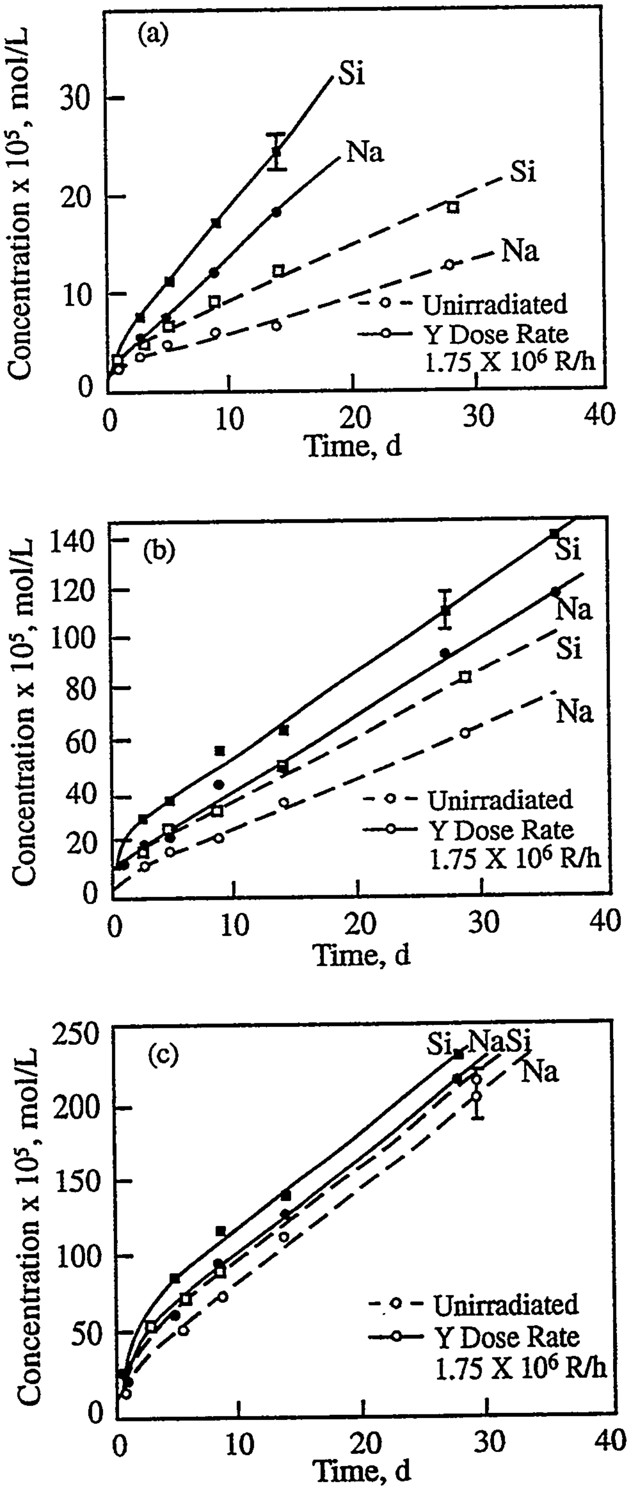

Fig. 2-35. Na and Si Concentrations in Gamma–Irradiated vs. Nonirradiated Static Leach Tests with PNL 76-68 Glass Reacted in Deionized and Deaerated Water. (a) 50°C trends, (b) 70°C trends, and (c) 90°C trends (adapted from [PEDERSON-1983c]). Test S/V ratio at 20 m^{-1}.

Significant changes in leachate pH and glass dissolution rates were not observed when glass samples were irradiated in the presence of groundwater equilibrated with tuff. Changes in solution pH of these systems were either buffered by bicarbonate in solution and/or the radiogenic acids were diluted under the relatively low S/V conditions of some of the tests [BIBLER-1985, -1986; VAN KONYNENBURG-1986; BATES-1987; ABRAJANO-1986, -1988a; EBERT-1987, -1990b, -1990c]. In a few tests, glass dissolution rates were actually reduced, relative to nonirradiated tests, when the samples were exposed to irradiated solutions [BATES-1986a]. Van Iseghem et al. [VAN ISEGHEM-1988b, -1990b, -1991] observed a decrease in the glass reaction rate resulting from a decreasing pH of 8.5 to 7.5 for glasses reacted in the presence of clay at a temperature of 90°C and a S/V ratio of 100 m^{-1}. The reduced pH led to a decrease in total Si solubility and, consequently, to a reduction in the release rate of other glass matrix components. Hench et al. [HENCH-1986c] also indicated that the effects of radiation are negligible in the presence of granite, bentonite, and silicate waters.

In tests conducted with alpha-emitting transuranic-doped glass, but without any external gamma exposure, glass dissolution rates increased up to three-fold relative to nonirradiated tests [MENDEL-1976; TURCOTTE-1981; BURNS-1982b; WEBER-1983a, -1983b, -1985]. Weber [WEBER-1991] notes that the dissolution rates from these studies were primarily determined from weight loss of the solids and, therefore, may underestimate the radiation-induced dissolution rates if reprecipitation of leached components has occurred.

Weber et al. [WEBER-1988] tested high alpha dose rates (^{238}Pu-doped glass) vs. low alpha dose rates (^{239}Pu- and ^{232}Th-doped glass) and found that the higher alpha radiation levels led to increased release rates of both Pu and Si from the glass by about a factor of two to three in both brines and deionized water at 10 m^{-1} 40°C (Fig. 2-36). Weber [WEBER-1988] identified a correlation between release rate increases and volume changes in the solids, suggesting a mechanistic relationship between glass dissolution and solid phase radiation damage.

By contrast, Bibler [BIBLER-1982a] compared actinide release rates in deionized water from high-activity ^{244}Cm-doped glasses (4×10^{18} alpha decays/cm^3) with relatively low-activity ^{239}Pu-doped glass (2×10^{14} alpha decays/cm^3). Both glasses displayed comparable release rates at 10 m^{-1} (^{244}Cm vs. ^{239}Pu release), suggesting that alpha decay damage had no effect on actinide release rates from the glass.

Vernaz et al. [VERNAZ-1991b] noted that Si concentrations in solution decreased slightly, whereas B, Ca, and Al concentrations were unaffected for glasses leached in 150°C solutions after exposures to 10^{18} to 10^{19} alpha decays/cm^3. Eyal and coworkers [EYAL-1985a, -1985b, -1987, -1989, -1990; OLANDER-1990a, -1990b] compared isotopic release rates of ^{238}U and ^{232}Th with their decay products ^{234}U, ^{230}Th, and ^{228}Th for powders with a mean particle diameter of ~1 μm, produced from a variety of naturally occurring silicate, phosphate, and oxide crystalline phases. Release rates of ^{228}Th and, to a lesser extent, ^{234}U were enhanced for most phases relative to the release rates of parent nuclides during corrosion tests in a bicarbonate solution at 25°C. Enhanced decay product release was attributed to increased chemical reactivity along alpha-recoil damage tracks and recoil ejection across the liquid-solid interface. No fractionation of ^{234}U from ^{238}U was observed in monazite, probably because the relatively long half-life of ^{234}U allowed the damage tracks to anneal prior to ^{234}U decay. Although annealing reduced overall release rates of U and Th, enhanced ^{228}Th/^{232}Th was detected, probably due to the rejection of ^{228}Ra from the mineral structure. For these samples, it appears that ^{228}Ra diffusion was enhanced during lattice repair. Similar studies examining the preferential release of decay products from glass samples have not been conducted.

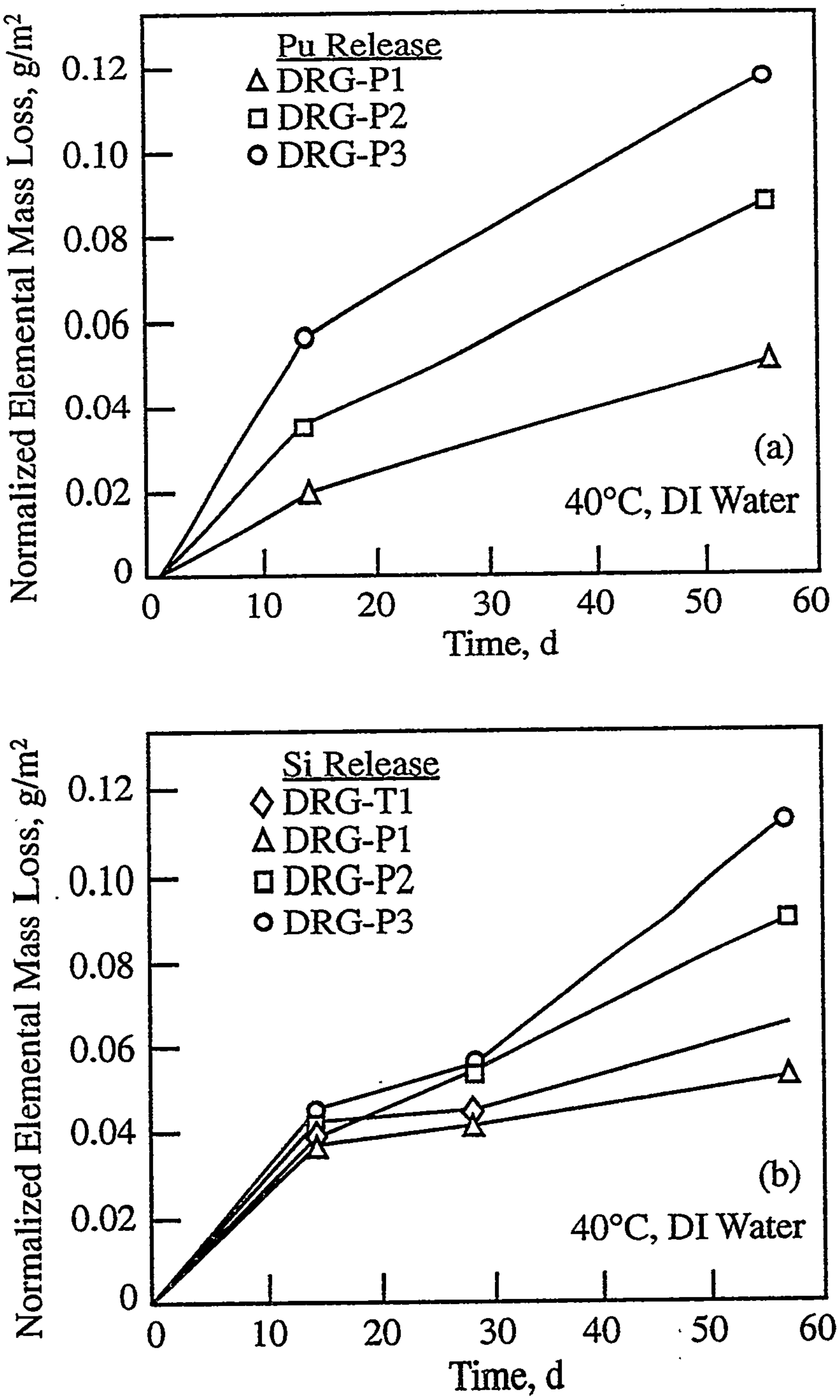

Fig. 2-36. Normalized Elemental Release Trends from Borosilicate Glass in Deionized Water MCC-1 Static Leach Tests as a Function of Time and Alpha Activity. Sample dopant levels (in oxide wt.%) as follows: DRG-T1, 1.0% $^{232}ThO_2$; DRG-P1, 1.0% $^{239}PuO_2$; DRG-P2, 0.9% $^{239}PuO_2$ + 0.1% $^{238}PuO_2$; DRG-P3, 1.0% $^{238}PuO_2$. (a) Pu release trends, (b) Si release trends (adapted from [WEBER-1988]).

Eyal and Olander [EYAL-1990] showed that less than 4% of the total Ra released from monazite samples over a 6.8-year test period was ejected from the solid directly by alpha-recoil processes. Burns et al. [BURNS-1982a] calculated the number of alpha-recoil atoms leaving the solid from the near-surface region relative to the total number of alpha decay events. The results indicated that atoms released by direct recoil represent a negligible fraction (1.5×10^{-21}) of the total alpha decays in the glass.

Several experiments have been devised to separately evaluate the influence of radiolytically produced nitric acid, carboxylic acid, and water dissociation products on glass dissolution. With tests in which nitric and carboxylic acid production were eliminated by vacuum degassing and Ar sparging, the radiation-induced release rate increases of B, Si, and alkalis were reduced to approximately half the rate increase that occurred when glass was irradiated in the presence of an air + water system [McVAY-1981a; PEDERSON-1983c]. McVay et al. [McVAY-1981a] also exposed glass samples to a nonirradiated deionized water + nitric acid test solution prepared at S/V ratios of 10 to 20 m^{-1} and pH of 3.5. This test simulated the glass exposure to radiolytically produced nitric acid without the exposure to water radiolytic products. Elemental release rates from these experiments were again about half as large as those of the irradiated air + water systems. These combined results indicate that both water radiolytic products and pH changes arising from acid production may be equally responsible for enhanced dissolution rates of glass observed in irradiated two-phase, air + liquid water experiments.

With experiments in which H_2O_2 was added in concentrations similar to levels expected during radiolysis, no measurable increase was noted in glass dissolution rates [McVAY-1981a]. Burns [BURNS-1982a, -1982b] suggested that the two most likely transient water radiolytic products responsible for accelerated glass leaching are the hydroxyl radical (•OH) and the molecular oxygen anion (O_2^-). The hydroxyl radical is favored as the dominant water radiolytic species responsible for accelerated glass dissolution because gamma radiolysis favors both radical species production and accelerates glass dissolution more than an equivalent dose exposure of alpha radiation [BURNS-1982b; PEDERSON-1983c].

Increases in redox potential of irradiated solutions may also lead to solubility changes in redox-sensitive elements such as actinides and some transition metals [MENDEL-1984; JANTZEN-1985c]. Nash et al. [NASH-1983] investigated the redox controls on Pu and Am dissolution and found that for irradiated glasses, Pu and Am release rates in a 25°C deionized water solution were increased five-fold relative to corresponding blank tests, whereas when glass disks were exposed to nonirradiated, dilute nitric acid solutions, release rates increased only two-fold over the blank tests. The increase in transuranic release was, therefore, attributed to a combination of radiolytically produced nitric acid and oxidation of the transuranics.

In most radiation studies, the leachant and glass were irradiated simultaneously, thus making it difficult to distinguish the effects of solid radiation damage from those of solution radiolysis. Mendel et al. [MENDEL-1984] devised experiments to separate the two effects by exposing borosilicate glass covered with a 25-µm layer of deionized water to an electroplated ^{238}Pu film. While the solution covering the glass was exposed to alpha radiation during testing, the glass was shielded from the alpha particles by the layer of water. No enhancement was noted in the growth rate of the hydrolyzed layer after 24 hours of exposure, as determined by secondary ion mass spectrometry depth profiling.

Boult et al. [BOULT-1978] irradiated alpha-doped glasses at 20°C for periods of one, two, and three years prior to their being exposed to leachant solutions in a Soxhlet leach test. The results indicated that release rates, based on total sample weight loss, increased about 50% for glasses irradiated for two years (about 4.7×10^{18} cumulative alpha decays/cm^3) relative to glasses irradiated for one year (about 2.5×10^{18} cumulative alpha decays/cm^3). No additional increase in release rate was observed for glasses subjected to three years of irradiation (about 7×10^{18} cumulative alpha decays/cm^3), an observation consistent with the solid damage saturation dose of 5×10^{18} alpha decays/cm^3 observed by Weber [WEBER-1982, -1984]. Malow et al. [MALOW-1980a] similarly noted minor increases in release rates, as determined by weight loss, for samples stored at temperatures of 50 to 170°C while receiving cumulative dose exposures of up to 3.3×10^{18} alpha decays/cm^3. In related studies, Ram et al. [RAM-1983] irradiated B-containing glasses with neutrons to produce the ^{10}B(n, alpha) ^{7}Li reaction, whereas Cousens and coworkers [COUSENS-1982, -1983] irradiated UO_2-containing glasses with neutrons to produce (n, alpha) and (n, fission) events. The former tests simulated a total exposure of about 3×10^{19} alpha decays/cm^3 without any observed increase in glass dissolution rates, whereas the latter tests resulted in release rate increases of two to four-fold for Li, Sr, and Si.

In studies where glasses were exposed to gamma irradiation prior to being immersed in a leachant solution, no significant increases were noted in release rates of alkalis, B, and Si over those of nonirradiated samples for cumulative doses from 10^7 to 4.6×10^{11} rad [KELLEY-1975; MENDEL-1976; BARKATT-1981b; McVAY-1981a, -1984; BIBLER-1982a, -1990a]. Other studies, however, have observed increases in dissolution rates up to four-fold after gamma irradiation of up to 10^{11} rad [GROVER-1973; BIBLER-1978].

Dran et al. [DRAN-1980, -1981] irradiated several types of glass with low-energy Pb ions to simulate the damage effects of recoil nuclei generated by alpha decay. In subsequent etching tests, etch pit development increased in damaged glass by a factor of 50-fold or more. In contrast, Manara et al. [MANARA-1982] noted only a four-fold increase in etch pit development on amorphous silica after Ne- and Ni-ion bombardment. Burns et al. [BURNS-1982a, -1982b] explained this difference by suggesting that the ion-irradiation studies of Dran et al. did not simulate a realistic repository leaching scenario because the ion irradiation produced overlapping zones having excessive damage and the glass did not have time to thermally anneal during the few minutes that the tests were run. Arnold et al. [ARNOLD-1982] and Petit et al. [PETIT-1989] also observed near-surface compositional changes in H, Li, Si, Na, and Nd in Pb-ion-irradiated glasses that were subsequently immersed in deionized water at 90 to 100°C.

Model simulations of ion-bombardment tests predict an increase in leaching as a result of spatial saturation effects at fluences of 10^{12} and 10^{14} ions/cm^2 [OUGOUAG-1984]. Also, the growth of stress has been found to be greatest for ion tracks that act on a planar surface, relative to an equivalent fluence resulting from internal alpha doping [OUGOUAG-1985]. These differences may offer an additional explanation for the large increase in dissolution observed in the ion-irradiation tests by Dran et al. [DRAN-1980, -1981].

Several studies have utilized both 2-3 MeV electrons and 0.5 MeV electrons to simulate the damage to waste glass as a result of beta irradiation [BONNIAUD-1977; BANBA-1980; ARAKI-1981; BURNS-1982a]. Studies at the upper energy range used a maximum cumulative dose of 1.2×10^{11} rad, whereas tests at the lower part of the range used a cumulative dose of 3×10^{11} rad. Subsequent dissolution tests did not show any detectable increase in elemental release rates for the irradiated samples relative to the nonirradiated glasses. A single exception to this trend was reported for the higher cumulative dose (3×10^{11} rad), low-energy electron-irradiated samples; in these samples, release rate increases, as measured by weight loss, were less than two-fold after a total fluence of 10^{19} e^-/cm^2 (Marples, unpublished data; referenced in Burns et al. [BURNS-1982a]).

Several issues need to be addressed by comparing the dissolution of fully radioactive versus simulated (nonradioactive) glass; including:

1. Do both glass types react through the same controlling mechanism?
2. Is there an atmospheric solution or solid-phase radiation or annealing effect that is not accounted for in tests with simulated glass and are the radiation conditions applied to evaluate the initial rate of glass reaction or long-term conditions similar to the conditions that will prevail under repository-relevant conditions?
3. Is there an element composition difference between glass types?
4. Is there a difference in secondary phases produced on the two glasses?
5. Is there a difference in durability between the two glass types?
6. What is the correspondence between the glass production, sample preparation, and test configurations used in the comparative tests?

Comparative tests between fully radioactive and simulated glasses were performed with an extensive test matrix that evaluated glass dissolution as a function of time (through one year), groundwater composition, temperature, flow, and the presence of engineered barrier system components [WERME-1990; JSS-1987, -1988]. Results for the simplest test comparison (deionized water, Ar atmosphere, static, S/V ratio of 1100 m^{-1}) showed that the B and Si release rate was about 50% greater from the fully radioactive glass (JSS/A) than from the simulated glass (ABS-118) after 91 to 180 days of reaction, although the difference in release rates diminished after 365 days (Fig. 2-37a). These differences are less than the factor of two reported for systematic errors with this data set, indicating that radiation did not have any significant effect on glass reactions under the Ar-atmosphere conditions of these tests. In a second comparison with an S/V of 10 m^{-1}, the fully radioactive JSS/A glass was reacted at 90°C and the simulated ABS-118 glass at 110°C (Fig. 2-37b). Based on the temperature difference, the simulated glass would be expected to react about four times faster than the radioactive glass (using the "rule of thumb" that for every 10°C increase in temperature, the reaction rate is estimated to double) [MENDEL-1981]). Although this expectation was met through 90 days, the B release rate for the simulated glass decreased significantly between 182 and 365 days whereas the release rate for the fully radioactive glass continued to increase linearly with time. When water flow was included as a test parameter, the general release trends were similar for both glasses, but there was a 40-day delay in the onset of release from the radioactive glass. Additionally, the B release trend of the simulated glass after 200 days appeared to be less than that of the radioactive glass.

. Comparative results are also available for tests in which 1 g of magnetite was included in the test vessel to simulate metal corrosion products. Through 182 days, the release rates for the radioactive glass were similar to or significantly less than those of the simulated glass, especially for relatively insoluble elements such as Al, Ca, and Sr. Tests were also done under static conditions with an S/V ratio of 1100 m^{-1}, and the results were even closer between the fully radioactive and simulated glasses than in the tests at the lower S/V ratio.

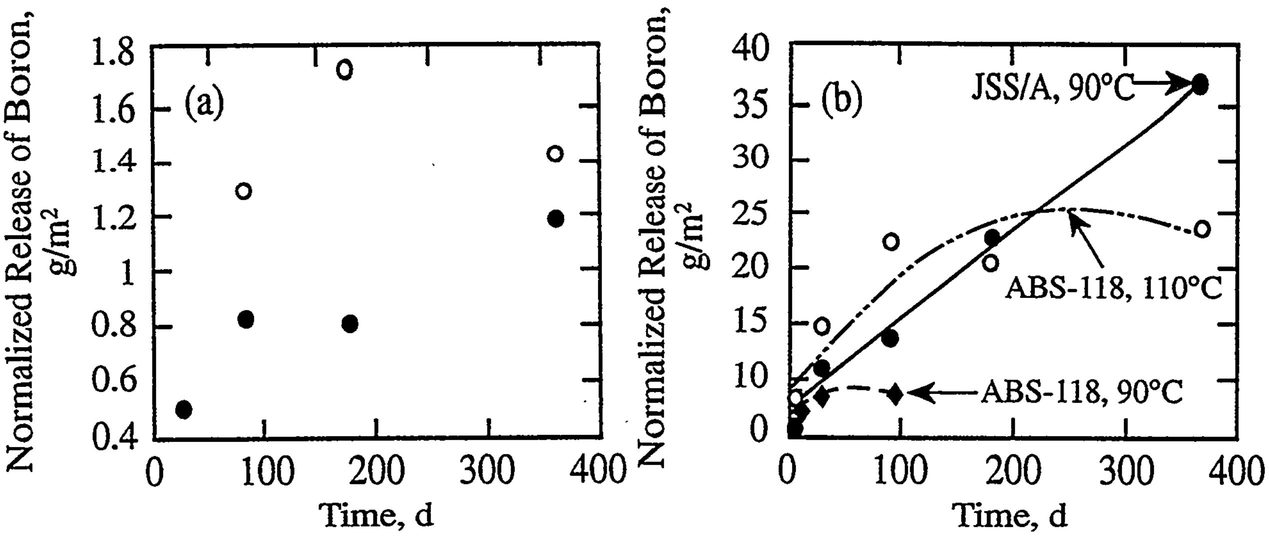

Fig. 2-37. Comparison of Normalized Boron Release from Batch Tests in Deionized Water for Fully Radioactive JSS/A (o) and Simulated ABS-118 Glass (•) (adapted after [JSS-1988]). (a) S/V = 1100 m^{-1}, 90°C, (b) S/V = 10 m^{-1}, tests at 90 to 110°C.

In the U.K., the release rates of the radionuclides Tc, Np, Pu, and Am were compared for fully radioactive glasses and actinide-doped simulated glasses with compositions representative of Magnox and THORP processes [HALL-1988; BOULT-1991; MARPLES-1991]. The differences in release rates were between two (Tc) and 75 times (Am), with the highest release rate from the fully radioactive glass.

To evaluate the behavior of fully radioactive glass under variable S/V conditions, Feng and Bates [FENG-1992b] and Bates et al. [BATES-1992d] compared reaction patterns for simulated vs. fully radioactive glass reactions in static conditions at 90°C at S/V ratios of 340, 2000, and 20,000 m^{-1}. The static tests were performed with fully radioactive and simulated SRL 131/11 and SRL 165/42 glasses that were previously studied by Bibler and SRL 200 glass that had been evaluated in short-term PCT tests [BIBLER-1990a, -1990b]. Differences in release rates for Si, Li, B, and Na were less than a factor of two to three between the simulated and fully radioactive tests run for reaction periods up to 182 days. The differences were attributed to the effect of radiation on the solution pH and dominant rate-controlling mechanism. For example, the SRL 165/42 glass displayed a slower pH rise than other glasses, with the fully radioactive SRL 165/42 glass showing a slightly lower initial pH relative to the simulated glass. A larger increase in alkali release occurred for the radioactive glass relative to the simulated glass, based on normalized release values (Fig. 2-38a).

For the SRL 131/11 and SRL 200 glasses, the solution pH was more basic, which favors a hydrolysis reaction process. The more basic the solution, the more rapid the hydrolysis reaction and the more rapid the reaction for the simulated glass (Figs. 2-38b and 2-38c). The differences in reaction rates between the simulated and fully radioactive glass were initially relatively small, and examination of the reacted glasses indicated that the structures of the reacted layers were similar. This comparison suggests that, although there is a difference in reaction rates between fully radioactive and simulated glass, the reaction processes are similar and thus glass performance can be modeled with confidence using data generated from simulated glass.

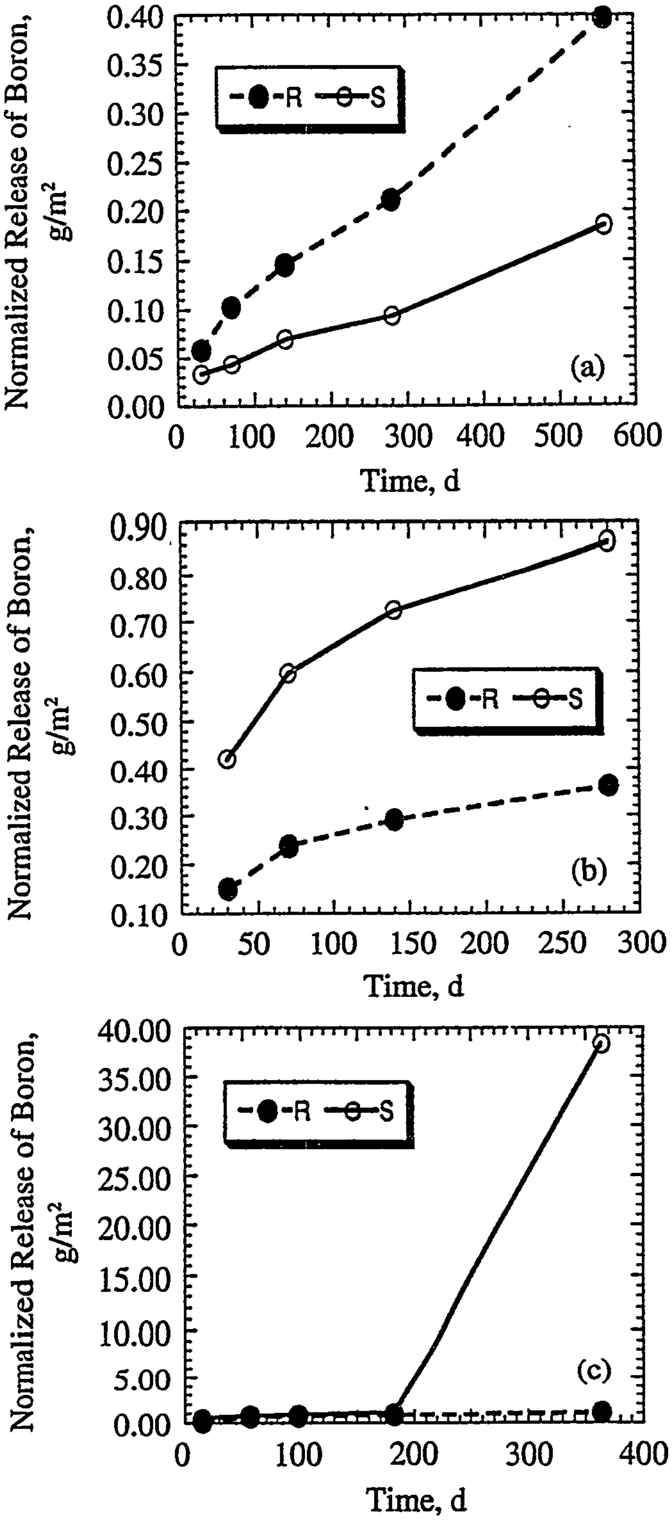

Fig. 2-38. Comparison of Normalized Boron Release from 90°C Batch Tests in EJ-13 Solution for Fully Radioactive (R) and Simulated (S) Savannah River Laboratory Glasses (adapted from [BATES-1992d] and [FENG-1992b]). (a) SRL 165/42 glass, S/V = 2000 m^{-1}, (b) SRL 131/11 glass, S/V = 2000 m^{-1}, (c) SRL 200 glass, S/V = 20,000 m^{-1}.

At longer reaction times, a difference in reactivity was observed between the simulated and fully radioactive SRL 200-based glasses (Fig. 2-38c). The simulated glass underwent rapid reaction between 182 and 364 days [BATES-1992d], and an increase in release of soluble components (B) was accompanied by the formation of distinct secondary mineral phases. However, the radioactive glass did not show a concomitant increase in B release or secondary phase nucleation. These results may be due to a slightly lower pH in the fully radioactive tests, which inhibits onset of the rapid reaction or the nucleation of secondary phases. More tests are needed to better understand the long-term effects of radiation on glass corrosion.

This work indicates that models used to predict long-term glass corrosion can be developed using the results of tests with simulated glass [WERME-1990]. However, such models must account for the effects of using fully radioactive glass, including the effects of radiation on the solution chemistry [BATES-1992d].

2.5.4 Summary

- The release rates of glass components into solution, including radionuclides, may be changed by the presence of radiolytically produced nitric acid, carboxylic acid, and transient water dissociation products such as •OH and O_2^-.

- In some tests, these radiolytic products increase the corrosion rate whereas in other tests they decrease the corrosion rate. The net effect depends on a complex balance between glass composition and environmental factors. For example, bicarbonate groundwaters may buffer against pH decreases and resultant leach rate increases arising from the formation of radiolytically produced acids.

- Radiation damage to solid glass materials results in bond damage and atomic displacements. Although such damage has been observed to increase dissolution rates by a factor of four under conditions where the damage is not annealed, glass annealing processes should negate most of the solid damage radiation effects arising from radionuclide decay under expected service conditions for waste glass.

- Tests using simulated glass compositions appear to simulate the behavior of fully radioactive glass samples, although additional tests are warranted in order to better understand the long-term effects of radiation on glass corrosion.

2.6 Microbial Effects on Borosilicate Glass Corrosion

The importance of microbiological activity on the rates and mechanisms of corrosion of glasses is relatively unknown. This is an area of concern for radioactive waste glasses because microbes may be capable of surviving in the radiation fields in the vicinity of the glass waste form. West [WEST-1986] showed that sulfate-reducing bacteria can survive in gamma fields up to 10^5 rad/hr and temperatures up to 80°C. Only recently have the effects of colonization of silicate and oxide surfaces by microorganisms begun to be studied. Previous work on microbial effects on the corrosion of solids has been driven mainly by practical problems of biofouling in ship's heat exchangers and hulls [DEMPSEY-1981].

Some work on microbial effects on natural glass dissolution has been performed. Thorseth et al. [THORSETH-1992] report observations of 1 micron-sized cyanobacteria occupying etch pits and porous (honeycombed) alteration layers on actively dissolving basaltic glass in seawater. The bacteria occur lumped together in discrete microcolonies which enhances their ability to optimize the microenvironment for their own benefit. Thorseth et al. propose that these bacteria may be affecting the glass dissolution rate by attaching to the glass surface and modifying the local environment, in particular by altering the pH, to promote breakdown of the glass structure and make available nutrients and metals (such as magnesium) for bacterial metabolism. Increasing the local pH to values above 9 increases the dissolution rate by at least an order of magnitude from near-neutral values. Typically, silicate minerals and glasses exhibit a minimum in dissolution rate at near-neutral pHs (Volume I, Fig. 3-3). Because pH has such a significant effect on dissolution rates, the ability of microorganisms to modify pH in their vicinity can have a major influence on mineral dissolution rates.

Other studies have investigated the effects of by-products of microbe metabolism on the dissolution of natural inorganic solids [BENNETT-1991; HEIBERT-1992; McMAHON-1991, -1992]. Microbes generate organic compounds including carboxylic acids that may act to solubilize metals though chelation. Heibert and Bennett [HEIBERT-1992] showed that silicon and aluminum were mobilized in a petroleum-contaminated quartz + feldspar sandstone aquifer in Minnesota because of complex organic acids generated by microbial activity which formed complexes with the silicon and aluminum. The organic acids increased the dissolution rates of quartz and feldspars in the aquifer. McMahon et al. [McMAHON-1992] showed that microbial metabolic activity (fermentation) in a clay and organic-rich rock at several hundred meters depth caused high concentrations of organic acids to accumulate in pore waters. Zones rich in microbes correlate with high porosity zones in these rocks. The authors postulate that microbial activity increases the dissolution rates and solubilities of minerals due to generation of organic acids which form aqueous complexes with elements contained in the minerals.

Microbes may also facilitate redox reactions involving iron, uranium, and other metals and affect mineral dissolution through catalysis of redox reactions at the glass surface [LOVLEY-1990; BARNES-1993].

It is likely that microbes will affect glass corrosion rates and mechanisms through the same mechanisms that they affect minerals. Borosilicate waste glasses contain many elements, such as iron and manganese, that undergo redox reactions which microbes enzymatically control in order to produce energy. Microbial effects may either enhance or retard dissolution rates through this process. The glass also contains elements, such as magnesium, that are important trace elements for microbes. Glasses may be preferentially attacked by microbes seeking these elements. Increased bacterial activity induced by the presence of glass surfaces, and in particular when nutrient levels were low, has been noted [LOOSDRECHT-1990]. Also, the glass may simply serve as an attachment site for microbes, as appears to be the case for cyanobacteria on natural basalts. Cyanobacteria need light to survive and this type of bacteria would therefore not be a problem in repository environments.

More work needs to be done to examine how important microbial effects may be on waste glass dissolution in repository environments. The effects are likely to be complex. For example, for any microbe that generates organic acids capable of enhancing glass dissolution through metal chelation, there are others that use the same organic acids as a food source. The overall effects of organic acid formation on glass dissolution rates will be determined by the relative production and decomposition rates caused by the two classes of microbes. Also, the microbially-induced enhanced dissolution of natural basalts observed by Thorseth [THORSETH-1992] was not a large effect.

Although the dissolution rate was increased by perhaps a factor of ten at the sites of bacterial attachment, the colonies were localized in restricted sites on the glass surface and were not globally distributed. The wide variety of microbe types and metabolic processes are such that competition between them serves to prevent large fluctuations in gross solution chemistry.

2.6.1 Summary

- The importance of microbiological activity on the rates and mechanisms of waste glass corrosion is relatively unknown. The effects may be associated with microbiological alteration of the local environment (particularly pH, redox, and organic complexant concentrations) at the glass surface. Quantitative information concerning the importance of these effects for nuclear waste glass is not available.

2.7 Radionuclide Release during Glass Corrosion

This section describes the behavior of radioactive constituents as the glass corrodes. All radionuclides are stabilized when incorporated into a glass matrix because their mobilization can only occur as the silicate network of the glass corrodes, and so their release from the waste form is limited by the glass corrosion. While the intrinsic resistance of borosilicate waste glasses towards corrosion is important in stabilizing the radionuclides and establishes a bounding upper limit on their release, several factors affect the subsequent mobilization and transport of radionuclides away from the waste form. These include the solubilities of the radionuclides and their complexes, colloid formation, and sorption onto other phases. Isotopes of Tc, U, Np, Pu, and Am are discussed in this section. The behavior of cesium and strontium is also discussed briefly. Although other radionuclides have been identified as potentially important (see Volume I, Section 2.1.2.3), their mobilization is not discussed beyond the constraints imposed by corrosion of the glass matrix.

The behavior of a radioelement upon glass corrosion is strongly influenced by its solubility. The total solubility of a particular element is given by the sum of the concentrations of all species of that element, including free ions, hydrolyzed species, and complexes, which are present in the solution. A maximum solution concentration of the uncomplexed species is established due to its equilibration with a solid phase. Solubility products have been measured for many actinide-bearing solids, although the phases which control actinide solubilities during glass corrosion are often difficult to identify. Maximum concentrations of complexes are established by their individual equilibria. In the absence of complexation, the solubilities of most actinides are generally quite low. Complexation generally leads to increased actinide solubilities, but may also result in decreased solubilities. Since the extent of hydrolysis and the concentrations of several ligands depend on the pH, the solubility of radioelements will also be pH-dependent. Complexation by ligands which are the conjugate bases of weak acids is not significant at pH values below the pK_a values of those acids. For example, carbonate is expected to be present in appreciable quantities only at pH values greater than about 10, bicarbonate above about pH 6, biphosphate above about pH 7, etc. The solubility may be affected by changes in the ionic strength, composition, and temperature of the solution [LEMIRE-1992]. Most laboratory investigations of actinide and technetium hydrolysis, complexation, and solubility have been performed at or near room temperature. Radionuclide behavior at elevated temperatures must currently be extrapolated from room temperature data or estimated from the behavior of nonradioactive homologs. Much thermodynamic information is still needed before the solubilities and complexation of transuranium elements can be utilized to reliably model long-term geologic interactions [FUGER-1992].

Technetium and the actinide elements may exist in solution in several oxidation states depending on the chemistry of the contacting solution. The effect of the redox potential of the solution on the preferred oxidation state(s) of an individual actinide is related to the reduction potential of that actinide, which depends on the temperature and ionic strength of the solution. Standard reduction potentials are typically measured at or near room temperature and are extrapolated to zero ionic strength and zero pH. The few studies conducted at different temperatures show that the solubilities are sometimes affected by temperature changes [e.g., LEMIRE-1993] and sometimes not affected [e.g., NITSCHE-1985a, -1985b]. Certainly, more experimental work is needed to properly account for temperature changes.

The chemistry of natural groundwaters and aquatic systems that may eventually contact high-level waste glasses can vary significantly depending on the surrounding environment (see Volume I, Section 2.2). Also, the chemistry of the fluids contacting the waste glass in the near-field environment will differ from the initial groundwater due to corrosion of waste glass and other materials in the engineered barrier system and radiolysis of the air and groundwater [LUTZE-1992; GRAMBOW-1991]. The pH of the groundwater contacting the waste glass will depend on the contributions of several simultaneous interactions. For example, it is expected to increase as the glass corrodes due to the release of alkali (although the pH of some brine solutions have been found to decrease during corrosion due to secondary phase formation [GRAMBOW-1990]), but will decrease due to the generation of nitric and nitrous acids through the radiolysis of moist air (see Section 2.5). Likewise, the redox potential of the solution will be affected by the release of redox-sensitive elements such as iron and the radioelements themselves from the glass and other materials during corrosion of other components of the waste package, and radiolysis of the air and groundwater. Therefore, the stabilities of actinide species in the near-field environment must be considered under a range of conditions much wider than those defined by potential groundwaters to interpret laboratory experiments and to model the long-term repository behavior in computer simulations.

While the concept of thermodynamically controlled radionuclide solubilities is useful in discussing actinide release, other interactions may significantly affect the distribution of radionuclides as the glass corrodes. Radionuclides may also sorb onto colloids occurring naturally in the groundwater or colloids generated during glass corrosion. In addition, radionuclides that are released from the glass into the groundwater may become incorporated in secondary phases that are generated as the glass corrodes, including altered layers at the glass surface and precipitated mineral phases, or they may sorb onto these phases or other materials in the vicinity of the waste form.

The potential distribution of radionuclides between mobile and immobile phases in the immediate vicinity of the corroding waste form is discussed below. Because the solubility and sorptive properties of the radioelements are strongly dependent on their oxidation states and complexation, the chemistry of technetium, uranium, neptunium, plutonium, and americium is first summarized (Section 2.7.1) to assist in the interpretation of various test results. Experimental observations of the interactions of these radionuclides with the altered glass layers, secondary mineral phases, and colloids near the surface of the corroding glass are then discussed in Sections 2.7.2 and 2.7.3.

2.7.1 The Chemistry of Technetium, Uranium, Neptunium, Plutonium, and Americium

This section summarizes which species are stable in aqueous solutions under different Eh and pH conditions and the interactions of these species with complexants that are common to groundwaters or which may be introduced into the groundwater solution by corrosion of the waste package or engineered barriers. This section is not intended to provide a complete review of the chemistry of these elements. Rather, the chemistry of the radionuclides is discussed with regard to redox behavior, hydrolysis, complexation, and solubility as measured in well defined systems to support discussions of leach test results in more complicated systems with actual groundwaters and waste glasses. While much of the behavior of actinides in actual groundwaters may be inferred based on their behavior in simple systems [ALLARD-1980; JENSEN-1988], discussions in Section 2.7.2 highlight experimental observations.

2.7.1.1 Standard Reduction Potentials of the Actinides

Representative standard potentials of the actinides are summarized in Table 2-9. For comparison, the standard potential to oxidize water to oxygen gas is about 1.6 V, and that to reduce water to hydrogen gas is 0 V by definition. Uranium is oxidized from the U(III) state to the U(IV) state in air (rapidly) and water (slowly), Np(III) is oxidized to Np(IV) in air (readily), and Pu(III) is oxidized to Pu(IV) (slightly) as a result of its own α-decay. Americium is stable in the Am(III) state except in strongly oxidizing solutions. Tetravalent U(IV) and Np(IV) are stable in water but are oxidized by O_2 to UO_2^{2+} and NpO_2^{+} in air; Pu(IV) is stable in acidic solutions at low concentrations, but disproportionates to Pu(III) and Pu(VI) at high concentrations. All actinides exist in the An(V) and An(VI) states, with the dioxo ions AnO_2^{+} and AnO_2^{2+} being important, although AmO_2^{2+} exists only under strongly oxidizing conditions. The relative stabilities of the AnO_2^{+} species decrease as Np(V), Am(V) > Pu(V) > U(V), with Pu(V) and U(V) disproportionating to the An(IV) and An(VI) states. Neptunium also disproportionates at low pH values and high concentrations. The relative stabilities of the AnO_2^{2+} species decrease as U(VI) > Pu(VI) > Np(VI) > Am(VI). Uranium(VI) is stable and difficult to reduce, while Pu(VI) and Np(VI) are more easily reduced. Am(VI) is a strong oxidizing agent and is readily reduced to lower oxidation states. The most stable oxidation states for the actinides in the pH range of about 5-10 under oxidizing conditions are U(VI), Np(V), Pu(V), and Am(III), while oxidation states of U(IV), Np(IV), and Pu(IV) may be stabilized upon complexation. The stable oxidation states under reducing conditions are U(IV), Np(IV), Pu(III,IV), and Am(III). The chemistries of the individual actinides are complicated by the possibility that several oxidation states may exist in solution simultaneously.

The valence of actinides in the waste glass will depend on the conditions under which the glass was formed, especially the oxygen partial pressure and the melting temperature. In the presence of air, the following valance states have been observed in borosilicate glasses: U(VI), Np(IV or V), Pu(IV), and Am(III) [ELLER-1985; VEAL-1987]. Technetium(VII) may be volatilized as alkali pertechnetates and as Tc_2O_7 under oxidizing conditions. Insoluble TcO_2 is precipitated in reducing glass melts [FREUDE-1989]. Technetium has been found on the surfaces of bubbles in the glass [BRADLEY-1979, pg. 7], which suggests that gaseous Tc_2O_7 forms during melting. However, the oxidation state that is stable in solution will be set by the reduction potential of the solution.

Table 2-9. Standard Reduction Potentials for Actinide Elements

Reaction	Standard Reduction Potential, V				Reference
	U	Np	Pu	Am	
$An^{4+} + e^- = An^{3+}$	-0.52	0.15	1.01	2.34	a
		0.21	1.015		b
				2.6	c
	-0.631	0.155	0.982	2.7	d
$AnO_2^+ + 4H^+ + e^- = An^{4+} + 2H_2O$	0.46	0.65	1.10	1.10	a
	0.58	0.739	1.172	1.04	d
				1.1	e
$AnO_2^{2+} + 4H^+ + 2e^- = An^{4+} + 2H_2O$	0.27	0.94	1.03	1.35	a
	0.32	0.938	1.043		d
$AnO_2^{2=} + e^- = AnO_2^+$	0.08	1.23	0.96	1.60	a
		1.162	0.954		b
	0.063	1.137	0.913	1.60	d
				1.6	e

[a] [ALLARD-1984].
[b] [RIGLET-1989].
[c] [HOBART-1982].
[d] [JONES-1969].
[e] [SCHULZ-1976].

2.7.1.2 Hydrolysis

All the actinides readily undergo hydrolysis as the solution pH increases, with the ease of hydrolysis increasing with the atomic number. The tendency to hydrolyze is related to the effective charge and radius of the ionic species, and decreases as $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$ [CHOPPIN-1983a]. The effective positive charges of the actinides in the linear actinyl(VI) and (V) species are interpreted by Choppin to be 3.3+ and 2.1+, respectively, based on correlation of thermodynamic data [CHOPPIN-1983b]. Hydrolysis can be represented by the equivalent generic reactions:

$$An^{n+} + H_2O = An(H_2O)^{n+} = An(OH)^{(n-1)+} + H^+ \qquad (21)$$

for which the hydrolysis constant is $K_{h1} = [An(OH)^{(n-1)+}][H^+]$. An equivalent reaction can be written by subtracting the water dissociation reaction as

$$\begin{array}{ll} An^{n+} + H_2O = An(OH)^{(n-1)+} + H^+ & K_{h1} \\ H^+ + OH^- = H_2O & -K_w \\ \hline An^{n+} + OH^- = An(OH)^{(n-1)+} & K_{h2} = [An(OH)^{(n-1)+}]/[OH^-] \end{array} \qquad (22)$$

such that $K_{h2} = K_{h1}/K_w$. From these reactions, the hydrolysis of the actinides is seen to be related to the acidities of the hydration complexes. For example, in the absence of complexing ligands, hydrolysis begins for Pu^{4+} at pH < 0, for PuO_2^{2+} at pH values between 4 and 5, for Pu^{3+} at pH values between 6 and 8, and for PuO_2^+ at pH values between 9 and 10 [CHOPPIN-1983b]. That is, $Pu(H_2O)^{4+}$ is a stronger acid than $PuO_2(H_2O)^{2+}$. Experimentally measured hydrolysis constants have been tabulated elsewhere [see, for example, ALLARD-1984; KIM-1986; IAEA-1992; AHRLAND-1991].

2.7.1.3 Complexation

Most actinide ions are readily complexed by a variety of ligands, including ligands commonly found in natural groundwaters. Natural groundwaters typically contain carbonate, fluoride, chloride, sulphate, and phosphate ions which may complex actinide ions. The amounts of these species present in different groundwaters vary widely, and specific ligands may or may not be present in appreciable quantities in the particular groundwaters of interest. The concentration of carbonate depends on the solution pH and contact with carbonate-containing minerals, such as limestone. The dissolution of carbon dioxide into the groundwater may also be important, depending on the degree of air exchange at particular repository sites. In a repository, nitrate and nitrite concentrations in the groundwater may increase due to radiolysis of the air, while fluoride, chloride, sulfate, and phosphate may be released into solution during glass corrosion. In general, the stabilities of the actinide complexes formed decreases as $CO_3^{2-} > PO_4^{3-} > F^- > SO_4^{2-} > HPO_4^{2-} > Cl^-, NO_3^-, NO_2^-$. Because of its high complexing strength and natural occurrence in most groundwaters, carbonate is a dominant ligand for solubilized actinides in natural groundwaters [SIMPSON-1980; KIM-1985]. Stability constants for inorganic complexes have been tabulated by several authors [see JONES-1969; CLEVELAND-1970a; PHILLIPS-1982; CHOPPIN-1985; NEWTON-1985a; KIM-1986; IAEA-1992].

Organic materials which occur naturally in the groundwater or which may be introduced in the repository horizon during excavation or other activities may also complex actinides in the near-field environment. While a variety of proteins, lipids, carbohydrates, and organic acids occur in groundwaters, the majority of organic material in many groundwaters are humic substances [CHOPPIN-1985]. Humic substances consist of organic materials that have decayed to such a degree that the parent material is no longer recognizable. Humic substances are generally classified as humic acids, fulvic acids, or humins according to their solubilities in acids and bases: Humic acids are insoluble in acids (pH values below about 3), fulvic acids are soluble in both acids and bases, and humins are insoluble at all pH values. They are naturally occurring, high molecular weight polyelectrolytes which may contain a large number of complex functional groups [HIGGO-1993]. The stabilities of organic actinide complexes are generally similar to those of analogous hydrolysis and carbonate complexes. Complexation with carbonate and humic acids and hydrolysis are competitive reactions in natural groundwaters, unless the concentration of one ligand predominates [KIM-1986].

In general, complexation with humic materials is more important for the An(III) and An(VI) states while the hydrolysis of An(IV) may be more important [CHOPPIN-1992; MOULIN-1992a, -1992b]. In addition, complexation with humic materials may result in a reduction in the oxidation state of the bound actinide [SKOGERBOE-1981; NASH-1981; CHOPPIN-1985, -1992; MOULIN-1992c].

Complexation is described in terms of stepwise stability constants, which, for a generic reaction between the metal ion M and the ligand L

$$ML_{n-1} + L = ML_n \tag{23}$$

can be written as

$$K_n = [ML_n]/[ML_{n-1}][L] \tag{24}$$

The overall stability constant for the reaction

$$M + nL = ML_n \tag{25}$$

is given as

$$\beta_n = [ML_n]/[M][L]^n = \Pi_n K_n \tag{26}$$

The relative strengths of complexes formed with actinides in various oxidation states with several ligands are summarized in Table 2-10, based primarily on values presented in [IAEA-1992] and [KIM-1986; ANDERSSON-1989]. The ranking of complexes as very strong, strong, moderate, weak, or very weak was assigned according to the formation constants for the 1:1 complexes. The stepwise stability constants for complexation with additional ligands is usually similar to that with the first ligand. In some cases, only values for higher complexes were available. In these cases, those values were used to assess the complex strength. The values of the constants used to discriminate between various assigned strengths were selected only to conveniently group the data. This table shows the general complexation strength to decrease as OH^-, CO_3^{2-} > humic and fulvic acids > PO_4^{3-} > F^- > SO_4^{2-} > HPO_4^{2-} > Cl^-, NO_3^-, NO_2^-. The speciation of uranium, neptunium, plutonium, americium, and technetium complexes is discussed in more detail below.

2.7.1.3.1 Uranium

Uranium may exist in solution in oxidation states of U(IV), U(V), or U(VI). As it is a very strong reducing agent, U(III) is difficult to maintain in solution. The U(IV) and U(V) states exist under reducing conditions and under acidic pH values, although the stability field of pentavalent uranium (as UO_2^+) is small. In the absence of other complexants, such as carbonate and phosphate, tetravalent uranyl hydroxides such as $U(OH)_3^+$ and $U(OH)_4(aq)$ (and possibly $U(OH)_5^-$) are the dominant species in solution under neutral and basic conditions [RAI-1990]. In the presence of

Table 2-10. Summary of Formation Constants[a] for the Reaction $M^{m+} + L^{n-} \rightarrow ML^{m-n}$

Ligand	OH^-	CO_3^{2-}	$H_2PO_4^-$	HPO_4^{2-}	F^-	SO_4^{2-}	NO_3^-	NO_2^-	Cl^-	Humic or Fulvic Acid
U^{4+}	vs	vs		vs	s	s[e]	m		m	vs
UO_2^+		s								
UO_2^{2+}	s	vs	m, m[b]	s	s	m,[e]s[d]	w		m	vs
Np^{3+}	s	s	m						w	
Np^{4+}	vs	vs		vs	s	s[e]	m		m	vs
NpO_2^+	m	s	m	m, s[c]	m	m	w	w	w	m
NpO_2^{2+}	s	vs	m		s	m	w		m	vs
Pu^{3+}	s		m			s	m		m	vs
Pu^{4+}	vs	vs		vs	s	s[e]	m		m	vs
PuO_2^+	m	vs	m	m		m			w	s
PuO_2^{2+}	s	vs	m		s	m	w		m	vs
Am^{3+}	s	s	m	s	m	s	m	m	m	vs
Am^{4+}		vs								
AmO_2^+	m	vs	m							
AmO_2^{2+}							m			

[a] Designation of complex strength:
where $\beta = [ML^{m-n}] / [M^{m+}][L^{n-}]$

vs:	very strong	$\log \beta > 10$
s:	strong	$10 > \log \beta > 4$
m:	moderate	$4 > \log \beta > 0$
w:	weak	$0 > \log \beta > -4$
vw:	very weak	$-4 > \log \beta$

[b] $L = H_3PO_4$.
[c] $L = PO_4^{3-}$.
[d] $L = SO_3^-$.
[e] For reaction $M^{m+} + HSO_4^- \rightarrow MSO_4^{(m-1)+} + H^+$.

carbonate, $U(CO_3)_5^{6-}$ and $U(CO_3)_4^{4-}$ [BRUNO-1989] are formed via reduction of $UO_2(CO_3)_3^{4-}$ [CIAVATTA-1983]. Tetravalent uranium complexes strongly with HPO_4^{2-} [SCHREYER-1954; MOSKVIN-1967] and weakly with polyphosphate, $H_2P_2O_7^{2-}$. Strong sulfate-U^{4+} complexes also form with one or two sulfate groups [RAO-1969]; fluoride, chloride, and nitrate also complex tetravalent uranium [IAEA-1992].

Pentavalent uranium is unstable and rapidly disproportionates into U(IV) and U(VI). It may be stabilized in carbonate media, however, and the species $UO_2(CO_3)_3^{5-}$ has been identified as the limiting U(V) carbonate complex [FERRI-1983; CAPDEVILA-1990].

The U(VI) state is the dominant stable state under oxidizing conditions at all pH values and under slightly reducing to reducing conditions at higher pH values. The dioxo uranyl ion, UO_2^{2+}, is the dominant species at low pH values, although $U_2O_5^{2+}$, $U_3O_8^{2+}$, $U_3O_8(OH)^+$ and $U_3O_8(OH)_2$ form as the pH increases [SUTTON-1949; WEIGEL-1985]. Polymeric hydroxo complexes $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ have also been found at high solution concentrations under acidic conditions [KRAMER-SCHNABEL-1992; KIMURA-1992]. Anionic complexes such as $(UO_2)_3(OH)_7^-$ may be important at high pH values [KRUPKA-1985]. In the presence of carbon dioxide and under neutral and basic conditions, $UO_2(CO_3)_2(H_2O)^{2-}$ and $UO_2(CO_3)_3^{4-}$ are the dominant species in solution [WEIGEL-1985; KIMURA-1992]. The polynuclear hydroxycarbonate $(UO_2)_2(OH)_3(CO_3)^-$ has also been reported [MAYA-1982].

Hexavalent uranium as uranyl complexes strongly with HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4 [SCHREYER-1954]. Uranyl phosphates are also more soluble than uranyl hydroxides. Strong sulfate [WALLACE-1967; PATIL-1976] and fluoride [PATIL-1976; CHOPPIN-1984] complexes, and weaker polyphosphate ($H_2P_2O_7^{2-}$), chloride, and nitrate complexes form with hexavalent uranium [IAEA-1992]. Uranyl has also been found to weakly complex with silicic acid to form the $UO_2OSi(OH)_3^+$ species ($\log \beta = -2.4$) [SATOH-1992].

Both tetravalent and hexavalent uranium are strongly complexed by humic acids; the humic acid complexes form in preference to the carbonate complexes [NASH-1981; SHANBHAG-1981].

2.7.1.3.2 Neptunium

Trivalent neptunium is stable in solution under reducing conditions, with Np^{3+}, $NpOH^{2+}$, $NpCO_3^+$ and $Np(CO_3)_3^{3-}$ dominating the solution at increasing pH values. Phosphate complexes Np^{3+} as $Np(H_2PO_4)_n^{(3-n)+}$, with n = 1, 2, or 3 [MOSKVIN-1969a], and weak chloride complexes also form [IAEA-1992].

Tetravalent $Np(OH)_4$ and $Np(OH)_3^+$ are stable under mildly reducing conditions, while $Np(OH)_2(CO_3)_2^{2-}$ (or $Np(OH)_4(HCO_3)_2^{2-}$) and $Np(OH)_4(CO_3)_2^{4-}$ are stable at high carbonate concentrations [PRATOPO-1990, -1991]. Sulfate complexes Np^{4+} with one or two sulfate groups [PATIL-1973]. Phosphate, fluoride [PATIL-1975], chloride, and nitrate also complex tetravalent neptunium [IAEA-1992].

The pentavalent dioxo species NpO_2^+ dominates under oxidizing conditions at low to neutral pH values. Because of its low electrical charge, NpO_2^+ is stable against hydrolysis to about pH 9 [LIERSE-1985], stable against complexation with carbonate to about pH 7.5 [KIM-1992], and is only weakly complexed by humic acids [KIM-1991a]. The species NpO_2OH, $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$ dominate above these pH values in solutions having high carbonate contents

[MAYA-1983; BIDOGLIO-1985]. The NpO_2^+ ion is complexed by phosphate [MOSKVIN-1964], sulfate [HALPERIN-1983], and weakly complexed by fluoride [SAWANT-1985; CHOPPIN-1984], chloride, nitrate, and nitrite [IAEA-1992]. The disproportionation of NpO_2^+ to Np^{4+} and NpO_2^{2+} is important in acid solutions [LIESER-1988]. Cation-cation complexes of NpO_2^+ with NpO_2^+, NpO_2^{2+}, and UO_2^{2+} have also been found [STOUT-1993].

Hexavalent neptunium is stable as NpO_2^{2+} and hydrolyzes to $NpO_2(OH)^+$ and as polynuclear species $(NpO_2)_2(OH)_2^{2+}$ and $(NpO_2)_3(OH)_5^+$ under highly oxidizing conditions and at low pH values [CASSOL-1972; GRENTHE-1986], while $NpO_2(CO_3)_2^{2-}$, $NpO_2(CO_3)_3^{4-}$, $NpO_2(OH)_2(CO_3)^{2-}$ and the polynuclear $(NpO_2)_2(OH)(CO_3)_3^-$ are the dominant solution species at high carbonate concentrations [MAYA-1984]. Raman spectra support the existence of $(NpO_2)_2(OH)_2^{2+}$ [MADIC-1984]. NpO_2^{2+} is complexed by phosphate [MOSKVIN-1964, -1969b], sulfate and fluoride [AL-NIAMI-1970a; CHOPPIN-1984], and weakly complexed by chloride and nitrate [AL-NIAIMI-1970b; IAEA-1992].

Neptunium(VI) is also strongly complexed by humic acid and is rapidly reduced to Np(V) upon complexation [NASH-1981]. The formation constants for complexes of Np(V) with several aliphatic and aromatic carboxylates have been measured to be weaker than the humic acid complex [TOCHIYAMA-1992].

2.7.1.3.3 Plutonium

Under reducing conditions, trivalent plutonium species such as Pu^{3+}, $PuOH^{2+}$, $PuCO_3^+$, $Pu(CO_3)_2^-$, and $Pu(CO_3)_3^{3-}$ are stable at increasing pH. Strong sulfate complexes $Pu(SO_4)^+$ and $Pu(SO_4)_2^-$ [FARDY-1976], weak chloride complexes $PuCl^{2+}$ and $PuCl_2^+$ [MARCUS-1966], and weak nitrate complexes with up to three ligands [LAHR-1970] have been reported.

Tetravalent $Pu(OH)_4$ is the dominant solution species under slightly oxidizing conditions at near-neutral pH values (minor amounts of $Pu(OH)_3^+$ and other hydroxides are also formed), while small amounts of carbonates including $PuCO_3^{2+}$, $Pu(CO_3)_2$, $Pu(CO_3)_3^{2-}$, $Pu(CO_3)_4^{4-}$, $Pu(CO_3)_5^{6-}$, and $Pu(OH)CO_3^+$ form at higher pH values [KIM-1986]. Tetravalent plutonium may form complexes with one to five HPO_4^{2-} ligands [DENOTKINA-1960; CLEVELAND-1970a, -1970b]. Fluoride also appears to complex tetravalent plutonium [BAGAWDE-1976; NASH-1984a] to increase its solubility, while complexation with sulfate may decrease the plutonium solubility [CLEVELAND-1983a, -1983b]. Interaction with sulfate yields $PuSO_4^{2+}$ and $Pu(SO_4)_2$ complexes [PATIL-1973; FARDY-1974], although the second ligand may not be fully dissociated, so that $PuSO_4HSO_4$ is formed [NASH-1983]. Higher sulfato complexes may occur at high sulfate concentrations [CLEVELAND-1970a, -1970b]. Complexes of Pu(IV) with nitrate and chloride are of moderate strength [BAGAWDE-1976; LAHR-1970], although complexes with up to six chloride ligands have been reported for Pu(IV) [CLEVELAND-1970a, -1970b]. Auto-radiolytic oxidation of Pu(IV) to Pu(V) or Pu(VI) has been observed in brine solutions, with the final oxidation state being dependent on the NaCl concentration (and the Eh) of the brine [KIM-1987a; BUPPELMANN-1988].

Pentavalent Pu is important under more oxidizing conditions, with $PuO_2(OH)$ and PuO_2^+ being important solution species at low pH values and $PuO_2(CO_3)_n^{1-2n}$ complexes being important in basic solutions [BENNETT-1992]. Under oxidizing conditions Pu(V) disproportionates to Pu(IV) and Pu(VI) under slightly basic pH conditions or to Pu(III) and Pu(VI) under acidic conditions [MADIC-1984; GUILLAUMONT-1992; CAPDEVILA-1992]. Plutonium(V) is complexed by phosphate and sulfate [MOSKVIN-1979], and fluoride [SAWANT-1985], but is only very weakly complexed by chloride [IAEA-1992].

Hexavalent plutonyl and plutonium hydroxides such as $PuO_2(OH)^+$ and carbonates such as $PuO_2(CO_3)_2^{2-}$ are stable under moderately oxidizing conditions and basic pH values [KIM-1986; GUILLAUMONT-1992; JENSEN-1980]. Complexation of Pu(VI) with bicarbonate as $PuO_2(HCO_3)^+$ has also been suggested [SULLIVAN-1982]. Polynuclear species $(PuO_2)_3(OH)_5^+$ [GRENTHE-1986; OKAJIMA-1990, -1991], $(PuO_2)_2(OH)_2^{2+}$, and $(PuO_2)_4(OH)_7^+$ [MADIC-1984] have been reported. Hexavalent Pu complexes strongly with fluoride [SAWANT-1985; CHOPPIN-1984], phosphate [DENOTKINA-1967; MOSKVIN-1969b], and sulfate [PATIL-1976], and weakly with chloride [RABIDEAU-1961] and nitrate [LAHR-1970]. Hypochlorite ions formed due to radiolysis of brine solutions lead to the formation of Pu(OH)(ClO) and $PuO_2(ClO)_2$ species [PASHALIDIS-1993]. Hypochlorite ions formed by radiolysis lead to the formation of strong Pu(OH)(ClO) and $PuO_2(ClO)_2$ species [PASHALIDIS-1993].

Both tetravalent and hexavalent plutonium are strongly complexed by humic acid, with Pu(VI) being reduced to Pu(IV) upon complexation [NASH-1981; JIANXIN-1993]. Pu(IV) may be further reduced to Pu(III) at pH below 3 [CHOPPIN-1992]. Auto-reduction of Pu(VI) to Pu(IV) has also been observed in carbonate solutions [LIERSE-1985].

2.7.1.3.4 Americium

Trivalent americium is stable under both reducing and oxidizing conditions; pentavalent and hexavalent species are stable only under highly oxidizing conditions in basic solutions. Trivalent carbonate complexes such as $AmCO_3^+$, $Am(CO_3)_2^-$, and $Am(CO_3)_3^{3-}$ [MOULIN-1988; NITSCHE-1989], and $Am(CO_3)_2^-$ are the dominant species in solution under basic conditions when carbonate is present [FELMY-1990], while uncomplexed Am^{3+} and hydroxides such as $AmOH^{2+}$, $Am(OH)_2^+$, and $Am(OH)_3$ dominate in solutions with low carbonate concentrations [STADLER-1988; MOULIN-1988]. Sulfate [McDOWELL-1972], phosphate [RAO-1986], fluoride [AZIZ-1969; NASH-1984b], nitrite, nitrate and chloride [KHOPKAR-1971] form one, two, or three ligand complexes with Am^{3+}. The autoradiolytic oxidation of Am(III) to Am(V) has been observed in brine solutions [MAGIRIUS-1985; KIM-1987a]. Americium(IV) is unstable with respect to disproprotionation, although Am(IV) can be stabilized in strongly complexing media [HOBART-1982].

Pentavalent AmO_2^+ and AmO_2OH (aq) are stable under highly oxidizing and basic conditions [STADLER-1988]. AmO_2^+ is also complexed by carbonate to form $(Am)_3(CO_3)_3$ [BOURGES-1983]. While the hexavalent AmO_2^{2+} species is stable under highly oxidizing conditions, carbonate complexes are not stable. Stable nitrate complexes have been reported [VASIL'EV-1975].

The high stabilities of humic acid complexes with trivalent americium are similar to those of carbonate complexes [KIM-1989a; CHOPPIN-1992].

2.7.1.3.5 Technetium, Strontium, and Cesium

The chemistry of technetium is dominated by the 4+ state in reducing solutions and the 7+ state in oxidizing solutions. While technetium may attain oxidation states from 2+ to 7+ in solution, oxidation states 3, 5, and 6 are unstable in most solutions. The standard potentials for technetium are summarized in Table 2-11. Technetium exists in solution as the divalent Tc^{2+} under highly reducing conditions, as tetravalent $TcO(OH)_2(aq)$, under mildly reducing conditions (TcO^{2+} is hydrolyzed to $TcO(OH)^+$ at about pH 1.3 and then to $TcO(OH)_2$ at about pH 2.2), and as the heptavalent

Table 2-11. Standard Reduction Potentials for Technetium[a]

Reaction	Standard Potential, V
$TcO_2(s) + 4H^+ + 4e^- = Tc(s) + 2H_2O$	0.27
$TcO_2(s) + 4H^+ + 2e^- = Tc^{2+} + 2H_2O$	0.14
$TcO_4^- + 2e^- = TcO_4^{3-}$	-0.60[c]
$TcO_4^- + 4H^+ + 3e^- = TcO_2(s) + 2H_2O$	0.74
$TcO_4^- + 6H^+ + 3e^- = TcO^{2+} + 3H_2O$	0.68 0.66[c]
$TcO_4^- + 3H_2O + 3e^- = TcO(OH)_2 + 4OH^-$	-0.050 -0.599[c]
$TcO_4^- + 4H^+ + 3e^- = TcO(OH)_2 + H_2O$	0.62 0.747[b] 0.595[c]
$TcO^{2+} + 2H^+ + 2e^- = Tc^{2+} + H_2O$	0.23

[a] [JENSEN-1980].
[b] [MEYER-1991a].
[c] [RARD-1983].

pertechnetate species (TcO_4^-) under oxidizing conditions. The pentavalent TcO_4^{3-} species exists in alkaline solutions, but disproportionates to Tc(VII) and Tc(IV); Tc(VI) may react with Tc(IV) to generate Tc(V), which may subsequently disproportionate [RARD-1983, pp. 28-35].

The solution chemistry of technetium depends on which oxidation state predominates, the positively charged Tc^{2+} or $TcO(OH)^+$, the neutral $TcO(OH)_2(aq)$, or the negatively charged pertechnetate ion. Pertechnetate is a weak base ($pK_b = -0.033$) [NAKASHIMA-1985]. Under aerobic (oxidizing) conditions, TcO_4^- is not readily complexed in solution, does not sorb onto most mineral surfaces or form pseudocolloids, and is not hydrolyzed, even at very high pH [LIESER-1987a, 1988]. Sorption occurs to a greater extent in anaerobic (reducing) conditions where $Tc(OH)_2$ (or TcO^{2+} or $TcO(OH)^+$) is the dominant species in solution. Tetravalent Tc(IV) is complexed by carbonate, sulfate, and halides, and colloids containing Tc(IV) have also been observed in acidic solutions [RARD-1983, pg. 66].

The chemistry of cesium is consistent with that of other alkali metals. It exists in the 1+ state, is highly soluble and not complexed. It readily ion exchanges with other alkali metals. Strontium behaves similar to calcium. It exists in solution in the 2+ state and is not complexed in solution. Insoluble carbonates are likely to form at high pH values.

2.7.1.3.6 Pourbaix Diagrams

The stability constants for various complexes can be used to predict the dominant solution species under specific solution conditions of Eh, pH, and complexant content. Competing redox, hydrolysis, and complexation reactions are accounted for and equilibrium concentrations are computed. Pourbaix diagrams are then generated by mapping the most abundant species on Eh/pH plots at constant temperature. Although several species may have similar thermodynamic stabilities under specific conditions, only the most stable species are included in the diagram. Diagrams have been generated considering only redox, hydrolysis, and carbonate complexation reactions [JENSEN-1980] and also considering various complexation reactions [PAQUETTE-1981]. Although the existence of many species identified in these diagrams has not yet been experimentally verified, these diagrams provide a useful representation of the speciation in complex systems having a large number of potential complexants. Of course, the speciation directly reflects and is restricted by the data base used in the computation, and the diagrams will likely evolve as more thermodynamic data become available.

Many competing reactions will occur within the fluids which contact high-level waste glasses, including hydrolysis, complex formation, and sorption, and the Pourbaix diagrams for these systems will be very complicated. Nevertheless, diagrams for simple systems accounting for only hydrolysis and carbonate complexes provide a useful basis for interpreting these more complex systems [KIM-1986].

2.7.1.4 Solubility

The solubility of a particular element is given by the sum of the concentrations of all species in solution, including free ions, hydrolysis species, and complexes. It may not be possible to experimentally determine solubility of a phase in natural groundwaters due to the presence of polymers and ultrafine colloids which cannot be removed from solution [KIM-1986]. The presence of such colloids will allow the solution contents of actinides to exceed their thermodynamic solubility limits. The concept of controlled solubility is nonetheless useful in discussing actinide release, and the added complication of colloid formation will be addressed separately in the context of experimental observations. Since the extent of hydrolysis and the concentrations of several ligands depend on the pH, the solubility will also be pH-dependent. For example, carbonate is present in appreciable quantities only at pH values greater than about 10, bicarbonate above about pH 6, biphosphate above about pH 7, etc. Therefore, complexation by these ligands is not significant at pH values below their pK_a values.

Thermodynamic solubility limits for radionuclides are established when the solution reaches equilibrium with a solid phase containing that element. For an oxide solid of a M(IV) species, a dissolution reaction can be written as

$$MO_2 + 2H_2O = M^{4+} + 4OH^- \tag{27}$$

and a thermodynamic solubility product defined as

$$K_{sp} = [M^{4+}][OH^-]^4 \tag{28}$$

While K_{sp} remains constant, the amount of M^{4+} that can exist in solution will vary inversely with the solution pH. In addition, M^{4+} may be oxidized or reduced, hydrolyzed, and complexed, such that total solubility of M in the solution may be much higher than the M^{4+} concentration. Note that the dissolution reaction may be written differently so that different values of K_{sp} are obtained. For example, the above dissolution of MO_2 may be written as

$$MO_2 + 4H^+ = M^{4+} + 2H_2O \tag{29}$$

for which

$$K_{sp'} = [M^{4+}]/[H^+]^4 \tag{30}$$

The two representations in Eqs. 27 and 29 are related by the water dissociation reaction as

$$\begin{array}{l} MO_2 + 2H_2O = M^{4+} + 4OH^- \\ 4H^+ + 4OH^- = 4H_2O \\ \hline \end{array}$$

$$MO_2 + 4H^+ = M^{4+} + 2H_2O \tag{31}$$

such that $K_{sp'} = K_{sp} K_w^4$.

Knowledge of the phases controlling the actinide solubilities in a repository setting is required to establish source values for performance modeling [NITSCHE-1991]. The solubility controlling phase may change with the Eh of the solution, and may be an oxide, carbonate, hydroxycarbonate, phosphate, or other solid. The solubility may also be affected by changes in the ionic strength, composition, and temperature of the solution [LEMIRE-1992], although the solubilities of Np, Pu, and Am at 25°C have been found to be similar to that at 60°C [NITSCHE-1987]. The phases formed in the complex fluids resulting from glass corrosion may themselves be highly complex, and may evolve with time as amorphous phases formed initially eventually crystallize.

While some solid phases formed in groundwater solutions have been identified [NITSCHE-1985b, -1991], much less is known about phases which form during glass corrosion (see Section 2.7.2 below). Some insight may be gained by considering the phases formed in simple systems. Measured solubilities of several technetium- and actinide-bearing phases are presented in Table 2-12. Most values have been extrapolated to zero ionic strength.

Table 2-12. Solubility Products of Some Solid Phases

Solid Phase Dissolution Reaction	Log Solubility Product (25°C)	Reference
U(III) $U(OH)_3 = U^{3+} + 3OH^-$	-19.29	[RAI-1978, pg. 91][a]
U(IV) $UO_2 + 4H^+ = U^{4+} + 2H_2O$	-1.8 -4.6 -1.6	[BAES-1976] [LEMIRE-1980] [BRUNO-1986]
$UO_2 + 2H_2O = U^{4+} + 4OH^-$	-60.6	[LANGMUIR-1978]
$UO_2 \cdot xH_2O(am) + 3H^+ = UOH^{3+} + (x+1)H_2O$	3.5	[RAI-1990]
$U(OH)_4 = U^{4+} + 4OH^-$	-46.23	[RAI-1978, pg. 91][a]
$UF_4 = U^{4+} + 4F^-$	-21.24 -24	[RAI-1978, pg. 91][a] [LEMIRE-1980]
$U(HPO_4)_2 \cdot 4H_2O = U^{4+} + 2HPO_4^{2-} + 4H_2O$	-26.8	[LEMIRE-1980]
$U(HPO_4)_2 = U^{4+} + 2HPO_4^{2-}$	-17.61	[RAI-1978, pg. 91]
$U(OH)_2 \cdot SO_4 = U^{4+} + SO_4^{2-} + 2OH^-$	-31.17	[RAI-1978, pg. 91][a]
$2U_4O_9 + 16H^+ + 3O_2 = 8UO_2^{2+} + 8H_2O$	169	[LEMIRE-1980]
$2U_3O_8 + 12H^+ + O_2 = 6UO_2^{2+} + 6H_2O$	70	[LEMIRE-1980]
U(VI) $\gamma\text{-}UO_3 + 2H^+ = UO_2^{2+} + H_2O$	6.8 7.7	[BAES-1976] [LEMIRE-1980]
$UO_3 \cdot 2H_2O + 2H^+ = UO_2^{2+} + 3H_2O$	5.6	[LEMIRE-1980]
$UO_2(OH)_2 + 2H^+ = UO_2^{2+} + 2H_2O$	5.6 5.7	[BAES-1976] [LEMIRE-1980]
$UO_2(OH)_2 = UO_2^{2+} + 2OH^-$	-22.2	[KRAMER-SCHNABEL-1992]
$UO_2CO_3 = UO_2^{2+} + CO_3^{2-}$	-14.2 -14.4 -13.29	[LEMIRE-1980] [GRENTHE-1984] [KRAMER-SCHNABEL-1992]
$3UO_2CO_3 + 6HCO_3^- = (UO_2)_3(CO_3)_6^{6-} + 3CO_2 + 3H_2O$	13.7	[GRENTHE-1981]
$(UO_2)_3(PO_4)_2 + 3H^+ = 3UO_2^{2+} + 2HPO_4^{2-}$	-24	[LEMIRE-1980]
$(UO_2)_2(HPO_4)_2 + 3H^+ = 2UO_2^{2+} + 2HPO_4^{2-}$	-23	[LEMIRE-1980]

Table 2-12 (Contd.)

Solid Phase Dissolution Reaction	Log Solubility Product (25°C)	Reference
Np(IV) $NpO_2 + 4H^+ = Np^{4+} + 2H_2O$	-4 -2.68	[BAES-1976] [RAI-1978, pg. 49][a]
$Np(OH)_4 = Np^{4+} + 4OH^-$	-55.22	[RAI-1978, pg. 49][a]
Np(V) $NpO_2OH = NpO_2^+ + OH^-$	<-9.2 -9.09	[BAES-1976 [RAI-1978, pg. 49][a]
$NpO_2OH(am) = NpO_2^+ + OH^-$	-8.8	[NECK-1992]
$NpO_2OH(aged) = NpO_2^+ + OH^-$	-9.4	[NECK-1992]
$Na_3NpO_2(CO_3)_2 = NpO_2^+ + 3Na^+ + 2CO_2^{2-}$	-14.16	[KIM-1986][b]
Np(VI) $NpO_2(OH)_2 = NpO_2^{2+} + 2OH^-$	≤-21.4 -22.70	[BAES-1976][b] [RAI-1978, pg. 49][a]
$NaNpO_2(CO_3) = NpO_2^{2+} + Na^+ + CO_3^{2-}$	-10.69	[KIM-1986][b]
Pu(III) $Pu(OH)_3 = Pu^{2+} + 3OH^-$	-19.7 -26.2	[CLEVELAND-1970b, pg. 311] [FELMY-1989]
$Pu(OH)_3 + 3H^+ = Pu^{2+} + 3H_2O$	22	[LEMIRE-1980]
$PuF_3 = Pu^{3+} + 3F^-$	-15.6 -10 -10.2	[CLEVELAND-1970b, pg. 329] [LEMIRE-1980] [ALLARD-1983][b]
$PuCl_3 + Pu^{3+} + 3Cl^-$	11.44	[RAI-1978, pg. 57]
$PuPO_4 = Pu^{3+} + PO_4^{3-}$	-23	[ALLARD-1983][b]
Pu(IV) $PuO_2 + 4H^+ = Pu^{4+} + 2H_2O$	-6.50 -7	[RAI-1978, pg. 57] [LEMIRE-1980]
$PuO_2 + 2H_2O = Pu^{4+} + 4OH^-$	-60.20	[KIM-1989b]
$2PuO_2 + 4H^+ + O_2 = 2PuO_2^{2+} + 2H_2O$	-1	[LEMIRE-1980]
$4PuO_2 + 4H^+ + O_2 = 4PuO_2^+ + 2H_2O$	-21	[LEMIRE-1980]
$4PuO_2 + 12H^+ = 4Pu^{3+} + 6H_2O + O_2$	-44	[LEMIRE-1980]

Table 2-12 (Contd.)

Solid Phase Dissolution Reaction	Log Solubility Product (25°C)	Reference
$Pu(OH)_4(am) = Pu^{4+} + 4OH^-$	-50.2 -57.85 -55.15	[RAI-1980b] [KIM-1989b] [CLEVELAND-1970b, pg. 311]
$Pu(OH)_4(am) + 4H^+ = Pu^{4+} + 4H_2O$	1	[LEMIRE-1980]
$Pu(OH)_2(CO_3) = Pu^{4+} + 2OH^- + CO_3^{2-}$	-68.8 -50.1	[KIM-1983] [KIM-1986]
$PuF_4 = Pu^{4+} + 4F^-$	-19.22 -13 -24	[CLEVELAND-1970b, pg. 333] [LEMIRE-1980] [ALLARD-1983][b]
$Pu(HPO_4)_2 = Pu^{4+} + 2HPO_4^{2-}$	-27.7 -28 -27	[DENOTKINA-1960] [LEMIRE-1980] [ALLARD-1983][b]
$K_4Pu(SO_4)_4 \cdot 2H_2O = 4K^+ + Pu^{4+} + 4SO_4^{2-} + 2H_2O$	-18.0	[CLEVELAND-1970b, pg. 433]
Pu(V) $PuO_2(OH)(am) + H^+ = PuO_2^+ + H_2O$	≤5.4 5	[BAES-1976] [LEMIRE-1980]
$PuO_2(OH) = PuO_2^+ + OH^-$	-9.30	[CLEVELAND-1970b, pg. 311]
Pu(VI) $PuO_2(OH)_2 = PuO_2^{2+} + 2OH^-$	-24.52	[CLEVELAND-1970b, pg. 312]
$PuO_2(OH)_2 + 2H^+ = PuO_2^{2+} + 2H_2O$	3	[LEMIRE-1980]
$PuO_2CO_3 = PuO_2^{2+} + CO_3^{2-}$	-12.77 -13.8 -12.77	[RAI-1978, pg. 57][a] [ALLARD-1983][b] [KIM-1986][b]
$PuO_2HPO_4 = PuO_2^{2+} + HPO_4^{2-}$	-13	[LEMIRE-1980]
$(PuO_2)_3(PO_4)_2 = 3PuO_2^{2+} + 2PO_4^{3-}$	-23.5	[ALLARD-1983][b]
Am(III) $Am(OH)_3 + 3H^+ = Am^{3+} + 3H_2O$	16.5	[SILVA-1983]
$Am(OH)_3 = Am^{3+} + 3OH^-$	-24.34	[BERNKOPH-1984, pg. 16]

Table 2-12 (Contd.)

Solid Phase Dissolution Reaction	Log Solubility Product (25°C)	Reference
$Am(OH)(CO_3) = Am^{3+} + OH^- + CO_3^{2-}$	-21.03 -22.5	[BERNKOPH-1984, pg. 156] [FELMY-1990]
$Am(OH)(CO_3) + 2H^+ = Am^{3+} + HCO_3^- + H_2O$	2.74	[SILVA-1983]
$NaAm(CO_3)_2 = Am^{3+} + Na^+ + 2CO_3^{2-}$	-20.2	[KIM-1986][b]
$Am_2(CO_3)_3 = Am^{3+} + 3CO_3^{2-}$	-19.1	[KIM-1986][b]
$AmF_3 = Am^{3+} + 3F^-$	-15.11	[RAI-1978, pg. 12][a]
$AmPO_4 \cdot xH_2O(am) = Am^{3+} + PO_4^{3-} + xH_2O$	-24.79	[RAI-1992]
Am(IV) $AmO_2 + 1.5H_2O = Am^{3+} + 3OH^- + 0.25O_2$	-52.99	[BERNKOPH-1984, pg. 125]
$Am(OH)_4 = Am^{4+} + 4OH^-$	-52.12	[RAI-1978, pg. 12][a]
Am(V) $AmO_2(OH) = AmO_2^{2+} + OH^-$	-33.29	[RAI-1978, pg. 12][a]
Am(VI) $AmO_2(OH)_2 = AmO_2^{2+} + 2OH^-$	-41.69	[RAI-1978, pg. 12][a]
Tc(IV) $TcO_2 \cdot 2H_2O(am) = TcO^{2+} + 2OH^- + H_2O$	-33.45 -32.8	[RARD-1983, pg. 46] [MEYER-1991b]
$TcO_2 \cdot xH_2O = TcO(OH)_2 + (x-1)H_2O$	-8.22	[ERIKSEN-1992]

[a] Value given in reference has been computed from other data.

[b] Assumed reaction. Reaction not given in reference.

Solid phases which may control the uranium solubility under different redox conditions include UO_2, $UO_2(OH)_2 \cdot H_2O$, and UO_2CO_3. The solids U_4O_9, U_3O_8, $Na_2U_2O_7$, and $NaUO_3$ have also been proposed to be solubility limiting phases [ALLARD-1984]. UO_2 is expected to be the solubility limiting phase under reducing conditions, and $UO_2(OH)_2$ under oxidizing conditions [NEA-1982]. Phosphate phases $(UO_2)_3(PO_4)_2 \cdot 6H_2O$, $UO_2HPO_4 \cdot 4H_2O$, and $UO_2(H_2PO_4)_2 \cdot 3H_2O$ have been identified in solutions with increasing phosphate concentrations [SCHREYER-1954]. A chloride-bearing phase, suggested to be $UOCl_2$, has been observed to decrease the uranium solubility in chloride solutions [AGUILAR-1991].

The neptunium solubility may be controlled by NpO_2, $Np(OH)_4$, NpO_2OH, or $NpO_2(OH)_2$, although NpO_2 is expected to be the solubility controlling phase under both oxidizing and reducing conditions [NEA-1982]. An amorphous hydroxide was found to control the solubility of Np(V) [ITAGAKI-1992]. The chemical state of the pentavalent hydroxide precipitate has been found to change from an amorphous solid upon precipitation to a crystalline solid after aging, where the time required for crystallization apparently depends on the ionic strength of the solution [NECK-1992].

The plutonium solubility may be controlled by trivalent plutonium as $Pu(OH)_3$ [FELMY-1989], tetravalent plutonium as PuO_2 or $Pu(OH)_4$ [KIM-1989b], or hexavalent plutonium as $PuO_2(OH)_2$ under oxidizing conditions. In the presence of high carbonate concentrations and at low pH values, PuO_2CO_3 may be the solubility limiting phase. Under reducing conditions, PuO_2 or PuO_2CO_3 are expected to be solubility limiting phase [NEA-1982].

The solid phase controlling the americium solubility may be $Am(OH)_3$, $AmOHCO_3$, or $Am_2(CO_3)_3$, depending on the carbonate content of the solution [NEA-1982; FELMY-1990; MEINRATH-1991; RUNDE-1992; VITORGE-1992]. Other solids may control the solubility of americium in the presence of other complexants, such as $AmPO_4 \cdot xH_2O(am)$ in phosphate containing solutions [RAI-1992].

The solubility of technetium (as $TcO_2 \cdot xH_2O$) is strongly dependent on the oxidation state of technetium in the solution: the pertechnetate ion is highly soluble while the Tc(IV) species have very low solubilities [LIESER-1987b]. Complexation of Tc(IV) to form carbonates and hydroxycarbonates above pH 8 increases the Tc(IV) solubility [ERIKSEN-1992].

Efforts have been made to predict the solubility and speciation of actinides in various repository waters [PRYKE-1985]. Model calculations are highly dependent on the accuracy of the data base used, of course, and so rely on experimental measurements of key redox potentials and solubilities in order to predict the behavior of more complicated systems. It should be mentioned that experimental measurements may be very sensitive to the system redox and pH, which may be difficult to control within the necessary tolerances. Experimental difficulties are reflected in the ranges of measured values seen in Table 2-12.

2.7.2 Radionuclide Behavior in Real Systems

2.7.2.1 Solubility, Speciation, and Complexation in Groundwaters

The solubility, speciation, and complexation of technetium and actinides will be strongly affected by the presence of other metals in actual groundwater solutions. Metal ions released during glass corrosion or during corrosion of other waste package materials or naturally occurring minerals within the host geology will compete for complexing ligands and will affect the redox properties of the solution. Several investigations in groundwaters representing potential repository sites have shown that the groundwater chemistry has a strong effect on the solubilities and speciation of radioactive elements. Some of these are discussed below.

The solubility and speciation of plutonium was measured in groundwaters from basalt, granite, shale, and tuff and in deionized water [CLEVELAND-1983c]. Solubility was the highest in basalt groundwater, intermediate in granite and tuff groundwaters, and lowest in deionized water and the shale groundwater. Plutonium was present as Pu(III), Pu(IV), and Pu(V+VI) in similar amounts. Differences were attributed to enhanced solubility in the basalt groundwater due to the formation of fluoride complexes and decreased solubility in the shale groundwater due to the formation of sulfate complexes. Dissolved oxygen, ionic strength, carbonate concentration, and pH were found to have little effect on the speciation.

The solubility of plutonium (IV) oxide in alkaline solutions representing Hanford waste solutions was determined as a function of NaOH, $NaAl(OH)_4$, $NaNO_3$, $NaNO_2$, and Na_2CO_3 concentrations [DELEGARD-1987]. The plutonium solubility was found to increase with the square of the NaOH activity, which was affected by the concentrations of the other salts. These results were interpreted by identifying $PuO_2(OH)_n^{(n-1)-}$ as being the dominant species in solution.

The simulated waste glass PNL 76-68 was reacted in a brine solution, in NaCl, $CaCl_2$, and $NaHCO_3$ solutions, and in deionized water (DIW) to assess the effects of the leachate composition on the release of silicon and doped Tc, U, Np, Pu, Am, and Cm from the glass [BRADLEY-1979]. The release rates were found to vary by an order of magnitude in the different leachants, where the release rates were highest in the bicarbonate solution and lowest in DIW. The general trend of the elemental release was Tc > Si, Np > U, Pu, Am, Cm in all leachants. Later tests in DIW, bicarbonate, and salt brine solutions showed that the releases of U (in salt brine and DIW), Np (in all solutions), and Pu (in DIW) were lower in deaerated solutions [PETERS-1981b]. Differences in the effect of deaeration on U, Np, and Pu may be due to different relative importances of carbonate complexes.

Steady-state leach rates of actinides from a sodium borosilicate glass reacted in a bicarbonate solution decreased as Np > Pu, Am under oxidizing conditions, but as Am > Np, Pu under reducing conditions, although the americium solubility was the same under both oxic and anoxic conditions [BIDOGLIO-1988a, -1988b]. The effect of the solution on the actinide solubilities are consistent with americium existing as Am(III) under both oxic and anoxic conditions, while neptunium and plutonium may exist as An(V) under oxic conditions and An(IV) under reducing conditions. Plutonium was also found to be associated with particulate matter under reducing conditions. The release into a brine solution was observed to fluctuate with time, and this was attributed to sorption onto a gel layer at the corroding glass surface [BIDOGLIO-1988a, -1988b].

The final oxidation states of Np, Pu, and Am in tuff groundwater (which is a reference groundwater for the proposed Yucca Mountain Site in Nevada, USA) became fixed at Np(V), Pu(V and VI), and Am(III), regardless of their initial oxidation states, and "hydroxide formation is not the principal factor controlling solubility in groundwater" [NITSCHE-1985b]. The solution concentrations of Np and Pu were higher in tuff groundwater than in deionized water, but the solution concentration of Am was lower in the groundwater. Complexation with carbonate probably increased the solubilities of Np and Pu, while complexation of Am did not occur at the pH of tuff groundwater used, which was reported to be 7 [NITSCHE-1985a, -1985b]. Comparison of two different tuff groundwaters showed the solubility of Np(V) to decrease and that of Am(III) to increase in the groundwater having the higher carbonate content; the solubility of Pu was similar in both groundwaters [NITSCHE-1992].

These results were attributed to control by sodium neptunium carbonates, americium hydroxycarbonates, and amorphous Pu(IV) polymers, the latter being unaffected by the carbonate content of the groundwater. Complexation by other components of the groundwater was reported to be less important.

The solubility of plutonium leached from a high level waste glass in both salt solutions and groundwaters representative of the Gorleben area in Germany were higher than predicted due to colloid formation [KIM-1985, -1987b]. The majority of actinides in solution have been found to be associated with humic colloids [DEARLOVE-1991]. Technetium was found not to interact with Gorleben groundwater under aerobic conditions, where pertechnetate is the dominant species in solution, but under anaerobic conditions, the technetium in solution as Tc(IV) was strongly sorbed onto mineral phases (predominantly quartz and silicates) present in the groundwater as colloids [LIESER-1987c]. Technetium was likewise found not to sorb onto sandy clays from the Gorleben area, but Cs^+ was strongly sorbed and Sr^{2+} moderately sorbed [BEHRENS-1982].

The release of technetium from a high level waste glass into a synthetic basalt groundwater (representative of the BWIP site in Washington, USA) was found to be high, but the solution concentration decreased after a short time in tests with basalt rock, probably due to the reduction to insoluble Tc(IV) [COLES-1984; WOOD-1987]. Other experiments with actinide-doped glasses showed the solution concentrations of the actinides to be low due to either their sorption onto test components or precipitation [COLES-1985; MEYER-1985; SCHRAMKE-1985]. Earlier measurements of actinide and technetium solubilities in basalt groundwaters with Umtanum basalt rock or Mabton Interbed materials showed the sorption of plutonium and americium to be similar under oxidizing and reducing conditions, while the sorption of neptunium and technetium was much greater under reducing conditions [SALTER-1982].

Laboratory experiments studying the interaction between Belgium waste glasses and Boom clay have shown that released plutonium and americium are strongly and almost completely sorbed onto the clay, such that only a minor fraction (about 0.2%) of released actinides remain mobile [LEMMENS-1993; VAN ISEGHEM-1993].

The interaction of technetium with granitic groundwaters was reported to be negligible under oxidizing conditions due to dominance of the anionic pertechnetate ion in solution [ALLARD-1979]. The solubilities of the actinides in a Swiss granitic groundwater have been modelled to be controlled by the dioxides of neptunium and plutonium, and either the dioxide or U_4O_9 for uranium [SCHWEINGRUBER-1982].

2.7.2.2 Interactions with Naturally Occurring Colloids and Mineral Surfaces

Colloidal material formed by naturally occurring inorganic and/or organic materials or microorganisms in the groundwater will be available to sorb radionuclides from the solution to form pseudocolloids that may remain suspended in the groundwater or may flocculate and settle out of solution [RAMSEY-1988; KIM-1991b; MOULIN-1992b]. Sorption may occur through dispersive interactions (physisorption), coulombic interactions (electrostatic adsorption and ion exchange), or electron exchange (chemisorption). The presence of colloids bearing radionuclides may lead to aqueous concentrations which exceed the solubility limits of pure phases. Colloids initially suspended in the groundwater may eventually be removed by interactions with geologic materials after longer times or as they migrate away from the waste form. Colloids may become filtered by micropores or may become sorbed onto mineral surfaces present in the host rock [LIESER-1987c; RIGHETTO-1988].

The sorption energy of the actinides onto mineral surfaces generally decreases as An(III,IV) > An(V) > An(VI). Uranium in the hexavalent state and neptunium in the pentavalent state are poorly sorbed onto most mineral surfaces, while tetravalent plutonium and trivalent americium are strongly adsorbed onto most geologic minerals. Sorption of radionuclides that exist in high valance states in solution may occur on sites capable of reducing the radionuclide to a lower oxidation state. Several studies have been performed to characterize the sorption of radionuclides onto mineral surfaces, both onto monolithic samples and onto mineral colloids. Some are discussed below.

The sorption of americium from a dilute J-13 groundwater solution onto tuff, romanechite (a manganese oxyhydroxide mineral), and clinoptilolite (a zeolite mineral) was measured in the pH range of 7-8 [TRIAY-1991]. The tuff (sample GU3-688 from borehole USW GU-3 at Yucca Mountain, NV) was composed of 68% alkali feldspar, 27% cristobilite, 4% quartz, and 1% smectite. Tests with rock showed that the sorption coefficient was 3.3×10^5 mL/g for romanechite, 1.2×10^4 mL/g for tuff, and 4.9×10^3 mL/g for clinoptilolite. Sorption coefficients are given as the ratio of g(An on sorbent)/g(sorbent) to g(An in solution)/ml(solution).

The interaction between granitic and bentonitic groundwater solutions with added technetium, uranium, neptunium, and plutonium and granite and gneiss rocks was studied under both oxic and anoxic conditions to assess the sorption and mobilities of these radionuclides [SUKSI-1989]. The sorption of uranium, neptunium, plutonium, and to a smaller extent technetium, was mineral-specific under oxic conditions. Except for uranium, precipitation of the actinides overwhelmed sorption under anoxic conditions. Neptunium was found to sorb onto minerals present in Finnish granite as Np(IV) under reducing conditions, but to be highly soluble as Np(V) under oxidizing conditions [HAKANEN-1991]. Plutonium and neptunium leached from doped Synroc was found to sorb onto mineral phases present in several Australian granites [GUTHRIE-1991]. The presence of the granites lead to a decrease in the oxidation potential of the solution and a higher pH, which decrease the solubility of both nuclides. Sorption was found to occur on leucoxene and iron oxides (hematite), sericite, chlorite and biotite, in decreasing order. Little sorption occurred on K-feldspar or quartz. Other tests with pure minerals commonly present in granite have shown uranium (as U(VI)) to be preferentially sorbed by goethite, hematite, and kaolinite, and slightly less so by chlorite and muscovite under normal atmospheric conditions [TICKNOR-1993]. Illite, calcite, quartz, epidote, and gypsum only weakly sorbed uranium under the same conditions. The sorption was less specific under less oxidizing conditions. Neptunium (as Np(V)) was strongly sorbed onto hematite, illite, chlorite, and calcite, and weakly sorbed onto kaolinite, epidote, and muscovite, but not sorbed onto quartz under an air atmosphere. The sorption of Np(V) was similar under less oxidizing conditions. The amounts of plutonium IV, V, and VI varied both with the total amount of dissolved solids (TDS) and the oxygen partial pressure. Pu(IV) dominated under conditions of low TDS and low oxygen conditions, while Pu(V,VI) were more important under low TDS and normal oxygen conditions. Plutonium was strongly sorbed onto hematite, illite, and kaolinite, moderately sorbed onto chlorite, goethite, muscovite, epidote, and calcite, and weakly sorbed onto quartz under both normal and reduced oxygen conditions, and at high and low TDS.

The solution pH will also affect the sorption of radionuclides onto mineral surfaces. The sorption of neptunium onto goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and boehmite (γ-AlOOH) was found to increase significantly above about pH 6-7, and the sorption onto hematite (α-Fe_2O_3), magnetite (Fe_3O_4), and biotite [($K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$] increased above about pH 8, although sorption onto α-Al_2O_3 showed no pH effect [NAKAYAMA-1991]. In tests with γ-Al_2O_3 colloids, the sorption of Am(III) and Np(V) were seen to increase suddenly at pH values near 5 and 7 [RIGHETTO-1988]. Plutonium (probably as Pu(V)) sorption on γ-Al_2O_3 colloids showed the same pH dependence in other tests [BIDOGLIO-1989].

Uranium and plutonium were strongly sorbed from deionized water solution onto colloidal bentonite clay, while neptunium was only slightly sorbed [SHADE-1984]. It was suggested that the weak sorption of neptunium may have been due to ferrous iron sorption sites. The sorption of actinides onto bentonite from an oxidizing granitic groundwater that had been preequilibrated with bentonite showed hexavalent uranium and pentavalent neptunium to sorb poorly onto finely ground bentonite ($K_d(U) = 0.093\ m^3/kg$; $K_d(Np) = 0.12\ m^3/kg$; $1\ m^3/kg = 1 \times 10^3\ mL/g$); reduced uranium and neptunium are expected to interact with bentonite more strongly [TORSTENFELT-1986a]. Tetravalent plutonium and trivalent americium were strongly sorbed onto bentonite ($K_d(Pu) = 3.5\ m^3/kg$; $K_d(Am) = 6.6\ m^3/kg$). Addition of iron or copper to bentonite increased the sorption of U, Np, and Tc onto bentonite, probably due to their reduction to U(IV), Np(IV), and Tc(IV); the sorption of Pu was not affected, probably because it was not further reduced from Pu(IV) [ALBINSSON-1991]. Sorption onto smectite and illite clays was also found to reduce Np(VI) to Np(V) [NASH-1981].

Sorption of Tc does not occur to an appreciable extent on mineral surfaces under oxic conditions. Little or no sorption of pertechnetate was measured on either anhydrite, basalt, granite, or tuff in tests conducted in rock cores, crushed rock columns, or in batch experiments with crushed rock [STRICKERT-1980]. In other tests conducted with 37 different mineral phases, including illite, kaolinite, and montmorillonite clay, the experimentally observed distribution coefficients were generally small and were attributed to ion-exchange [PALMER-1981]. Tests with colloidal iron silicate and bentonite showed no sorption of technetium under oxic conditions [SHADE-1984].

Technetium has been observed to sorb onto iron-oxide mineral inclusions in granite under anoxic conditions, however [VANDERGRAAF-1984; KUMATA-1993]. Ferrous iron is known to reduce pertechnetate to $TcO(OH)_2(aq)$ at pH values above about 6 [VANDERGRAAF-1984], and it is generally assumed that the pertechnetate ion must be reduced to Tc(IV) prior to sorption [ALLARD-1979; TORSTENFELT-1986b]. Technetium is also sorbed onto metallic iron, even in the presence of air. Technetium was found to strongly sorb onto sulfide minerals, including stibnite (Sb_2S_3), pyrrhotite (FeS), pyrite (FeS_2), galena (PbS), and loellingite ($FeAs_2$) under oxic solution conditions where pertechnetate is the dominant species in solution [BOCK-1989]. No Tc was sorbed onto colloidal silica, alumina, bentonite, or granite containing about 30-40% quartz and 26-35% plagioclase, 15-23% microcline, 8-11% hornblend, and less than 6% each biotite, chlorite, epodote, and others under a low oxygen atmosphere [SATMARK-1992]. These mineral surfaces apparently do not reduce Tc(VII). Rapid reduction of pertechnetate to Tc(IV) and subsequent sorption onto granite material in Sweden has been observed in both laboratory tests and in field tests [BYEGARD-1992]. Scavenging of Tc by iron hydroxide precipitates has also been reported to occur in tuff [BUDDEMEIER-1991].

Strontium and cesium are more strongly sorbed onto bentonite than is pertechnetate ($K_d(TcO_4^-) = 0.05$, $K_d(Cs^+) = 1.4$, $K_d(Sr^{2+}) = 2.9\ m^3/kg$), although the migration rates measured for Sr^{2+} and Cs^+ in bentonite are similar to that of pertechnetate [TORSTENFELT-1986b] Sorption of both onto silica colloids is very weak ($K_d(Cs^+, Sr^{2+}) \approx 0.05\ m^3/kg$), and sorption onto granite is stronger ($K_d(Cs^+, Sr^{2+}) \approx 10\ m^3/kg$) [SATMARK-1992].

In addition to actinides, sorption sites on mineral surfaces have an affinity for other solution species, including metal ions, complexants, and dissolved humic materials. Competition between different sorbants for surface sites and complexation of actinides in solution will affect the amount of actinides that may become sorbed onto mineral colloids in solution or minerals fixed in rocks. Competitive sorption of neptunium or plutonium and humic acid on γ-alumina, quartz sand and glauconite showed that binding of plutonium by humic acid decreased the retention of plutonium by the minerals [BIDOGLIO-1989]. The retention of neptunium by a column of crushed granite was also found to be reduced in the presence of humic substances [GUTIERREZ-1992]. The sorption of uranium and plutonium on London clay (38.4% illite, 17.9% quartz, 14.5% smectite, 13.3% kaolinite, plus chlorite, feldspar, calcite, dolomite, siderite, and pyrite) and Caithness flagstones (dominated by quartz, with calcite, feldspar, plagioclase, and pyrite) was studied in the presence of organic degradation products and gluconic acid [$CH_2OH(CHOH)_4CO_2H$] in deoxygenated, cement-equilibrated water (about 5×10^{-3} $\underline{M}$ Ca^{2+}, Na^+, and K^+) [BERRY-1991]. Gluconic acid was expected to simulate the complex organics, but the results showed gluconic acid to generally have a larger effect than the degradation products. Sorption onto clays was generally greater than sorption onto flagstones, and more filterable colloids were present in the tests with clays. Both gluconic acid and degradation products increased the sorption of plutonium onto the clay and both decreased the sorption of plutonium onto the flagstone. Interpretation of these results is complicated by pH effects and the presence of colloids [BERRY-1991].

The effect of humic acids on the leaching behavior of several metals, including uranium, from several glasses similar in composition to R7T7 show trivalent metal ions to be strongly complexed and solvated in the presence of humic acids, while tetravalent ions remained insoluble [DRAN-1992]. The importance of humic acid complexation is expected to decrease at pH values greater than about 8 [MOULIN-1992b].

2.7.2.3 Retention of Radionuclides by Glass Alteration Phases

The disposition of individual radionuclides between mobile and immobile phases as glass corrodes is strongly influenced by the solution chemistry and the presence of complexants and various sorbents. As presented above, technetium, uranium, and neptunium are generally more soluble than plutonium or americium in oxic solutions at the basic pH values expected in most repositories and attained in most tests, and are expected to attain higher solution concentrations in leach tests. Laboratory tests do show technetium, uranium, and neptunium to be released into solution to a greater extent than either plutonium or americium during corrosion of several glass compositions, including PNL 76-68 [BRADLEY-1979], R7T7 [FILLET-1985; VERNAZ-1992b], ATM-8 [BAZAN-1987; EBERT-1990b, -1990c], SRL 165 [EBERT-1990b, -1990c], and SRL 202 [BATES-1992b]. Likewise, higher solution concentrations of Cs than the less soluble Pu or Am were observed during leaching of SRP glass [BIBLER-1986], JSS-A glass [BJORNER-1988], and TOKAI glass [MIYAHARA-1988]. In other tests, technetium was found to be released congruently with boron under oxidizing conditions [BIBLER-1988b]. Actinides which do not enter solution due to low solubilities may be retained in the surface layers of the altered glass, either by sorption or incorporation into secondary phases, or may become sorbed on the surfaces of other materials that may be present in the vicinity of the corroding glass.

The retention of any element i during glass corrosion can be quantified by comparing the amount of that element in solution to the amount of boron in solution, as RF(i) = NL(B)/NL(i), where NL(i) is the normalized mass loss of element i [VERNAZ-1992b; TROTIGNON-1992]. Boron is assumed to be totally released into solution and to represent the extent of glass corrosion. High values of RF(An) indicate that actinides remain largely immobile as the glass corrodes, while low values indicate that mobilization of the actinides may occur as the glass corrodes. It should be emphasized that the retention factor is a measure of the release of actinides (and other elements) to solution relative to the release of boron and does not indicate the extent of glass corrosion. An RF(i) value close to unity simply means that element i is released from the glass at a rate similar to boron, which may be fast or slow. Indeed, changes in the retention factor under different experimental conditions is as much a measure of the effect of the test conditions on the boron release as it is a measure of the release of less soluble elements.

The release of uranium, neptunium, plutonium, and americium from R7T7 glasses into distilled water was measured in static leach tests with monolithic samples at S/V = 50 m^{-1} and at 90°C [VERNAZ-1992b]. Both the normalized boron release and the normalized actinide releases increased with the reaction time. Boron, uranium, and neptunium were dissolved in the leachates while most of the plutonium and americium in the leachate was present primarily as suspended material that was removed using a 25-nm filter. The suspended material is included in the released fraction. The measured retention factors are plotted in Fig. 2-39 for tests at 90°C run for between 1 and 364 days. All actinides are retained to some extent in the layer (i.e., log(RF) > 0 for all actinides), with the retention increasing as natural U, ^{237}Np < ^{238}Pu < ^{239}Pu < ^{241}Am. The retention factors for each

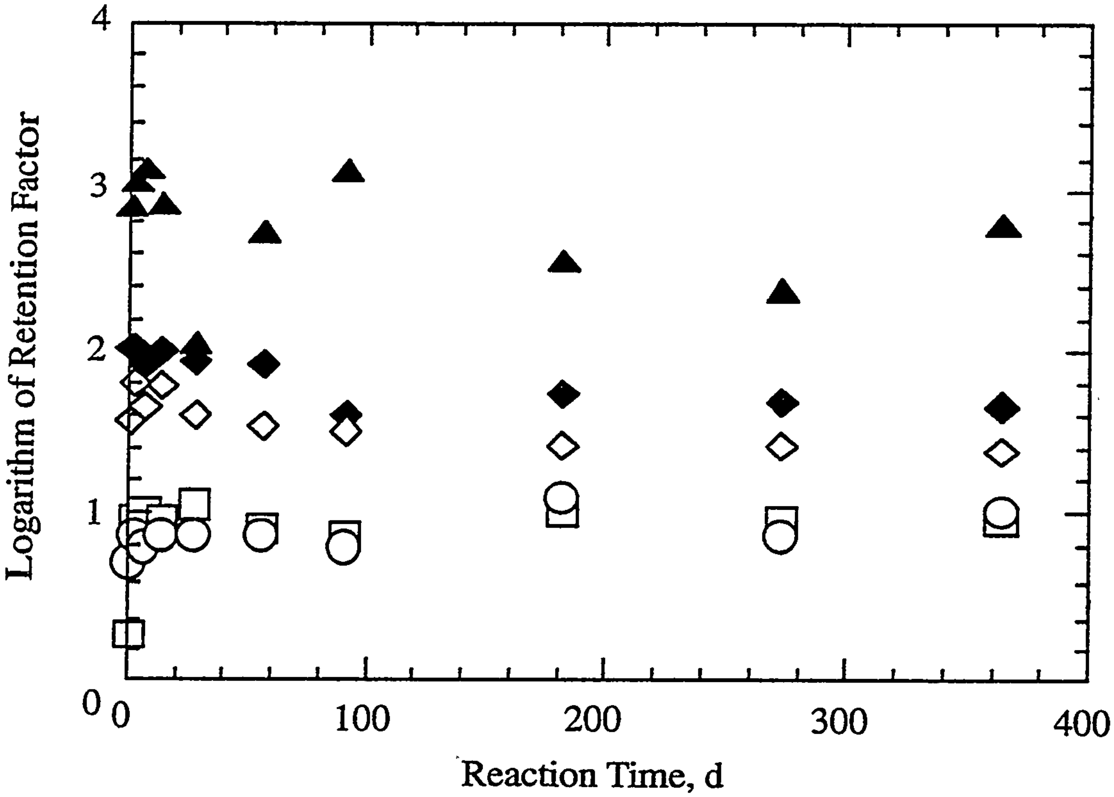

Fig. 2-39. Logarithm of the Retention Factors [RF_s] for Actinides Released from R7T7 Glass at 90°C (adapted from [VERNAZ-1992b]): (○) U, (□) ^{237}Np, (◇) ^{238}Pu, (◆) ^{239}Pu, and (▲) ^{241}Am.

actinide remain nearly constant for all times tested, although some scatter is present in the americium data due to the very low solution levels in the tests (which were between 1 and 15 ppb). The slight difference between ^{238}Pu and ^{239}Pu was attributed to radiolysis effects which resulted in a slightly lower pH in tests with ^{238}Pu. As the glass corrodes, only about 10% of the uranium and neptunium, 3% of the plutonium, and 0.3% of the americium is released into the solution, while the balance is retained in the altered surface layer. A similar suite of static leach tests was performed at 50°C. The retention factors of uranium and neptunium were similar in tests at 50°C and 90°C, while the retention factors of ^{239}Pu and americium were higher at 90°C. The release of both boron and plutonium was reduced by the low solution pH values, which were about 3 pH units lower in tests at 50°C with the ^{238}Pu-doped glass.

The preferred retention of plutonium and americium observed in static tests is consistent with tests performed under conditions where the leachate is continually refreshed and solubilities do not affect the amounts released. The integrated leach rates from R7T7 glass measured in Soxhlet tests at 100°C over 28 days were 2, 0.6, 0.005, and 0.003 g/m^2/day for boron, neptunium, plutonium, and americium, respectively [VERNAZ-1992b]. The higher release rate of neptunium compared to plutonium and americium is in agreement with the trend in the static tests as seen in Fig. 2-39. The release of actinides in the static tests was not limited by their individual solubilities, rather their release was correlated with and perhaps controlled by the glass corrosion rate.

The extent of accumulation of actinides in the altered layer will depend on the presence of other materials in the vicinity of the corroding glass onto which released actinides may sorb, such as clay backfills or metal barrier components. These materials may act as sinks to remove dissolved actinides from solution and provide additional barriers against radionuclide migration. Tests with R7T7 glass showed the amounts of Np and Pu retained in surface layers varied when other materials, including sand, granite, bentonite, smectite, illite, Boom clay, and salt were included in the test vessel [VERNAZ-1992b]. The presence of these materials also affects the solution chemistry and the glass corrosion rate [GODON-1989]. In general, the solutions in tests with the added materials contained more Np than those in tests with distilled water alone, but less Pu. Smectite, illite, and Boom clays sorbed Np (weakly) and Pu (strongly), granite and bentonite sorbed Pu (strongly), and salt sorbed Pu (weakly) [VERNAZ-1992b]. It was also found that the amount of plutonium in the altered layer remained high if the smectite was not in direct contact with the glass (RF(Pu) = 80), but was significantly reduced if the clay directly contacted the glass (RF(Pu) = 6) [VERNAZ-1992b]. This result is consistent with the affinity of the clay to sorb plutonium (see Section 2.7.2.2) and suggests that diffusion of plutonium through the solution limits the amount sorbed onto the clay surface.

Leach tests in a slurry of Boom clay showed retention of Np and Pu in layers formed on R7T7 glass and on a Pamela glass SM513, but a third glass, Pamela SM527, did not generate an alteration layer and did not retain these elements [LEMMENS-1993]. Technetium was not retained by the layers. The Pu and Am released from the glass were strongly sorbed onto the clay, while the Tc and Np were only partially sorbed onto the clay. The plutonium and americium had attained steady-state concentrations after two years of reaction (both below 2×10^{-9} $\underline{M}$) while neptunium was present at about 2×10^{-6} $\underline{M}$ and technetium at about 4×10^{-7} $\underline{M}$. Further, addition of Fe_2O_3 to the tests slowed the corrosion of all three glasses by at least a factor of 68 [LEMMENS-1993].

The redox state of the solution may affect the observed solubility and chemical behavior of the released actinides. Dynamic leach tests with borosilicate glass doped with Np, Pu, and Am were performed under oxidizing and reducing conditions [BIDOGLIO-1988a]. The steady-state solution concentration of Am was the same under both oxidizing and reducing conditions because Am(III) is the dominant oxidation state under both test conditions. On the other hand, Np(IV) and Pu(IV) were the dominant solution oxidation states under reducing conditions while Np(V) and Pu(V) dominated under oxidizing conditions. Because the solubilities of the An(IV) species are lower than those of the An(V) species, and the An(IV) species are sorbed more strongly within the altered layer, the solution concentrations of both Np and Pu were found to be higher under oxidizing conditions. Some reduction of Pu(V) was suggested to occur under oxidizing conditions [BIDOGLIO-1988b]. Likewise, the retention of uranium in the surface layer was greater after leaching in an anoxic atmosphere than in air [MANARA-1985]. The uranium solubility is expected to be greater in the presence of air due to formation of carbonate complexes [MANARA-1989]. Deaeration of deionized water, a bicarbonate solution, and a salt brine was previously seen to decrease the solution concentrations of Np, Pu and U in tests with PNL 76-68 glass [PETERS-1981b].

Identification of the solid phases which control radionuclide solubilities is required to accurately predict the radionuclide behavior during glass corrosion in repository setting. While phases controlling solubilities in pure systems may be identified by precipitation from supersaturated solutions [NITSCHE-1991], solubility-controlling phases are not easily identified in tests with waste glasses because most laboratory tests are performed using simulated glasses with low concentrations of radioelements, and the phases formed with radioelements are typically very small and interspersed with several other phases. Identification of phases containing radionuclides is complicated by the difficulties associated with handling radioactive samples and the limited sensitivity of analytical methods. Nevertheless, progress has been made in identifying phases formed which contain radionuclides.

Leach tests with relatively high uranium contents have lead to the identification of several uranium-bearing phases which form during glass corrosion. Weeksite, a uranium silicate, is the most commonly formed uranium-bearing mineral during glass corrosion [HARKER-1987; EBERT-1990a; EBERT-1991a]. Other uranium silicates have been found to form, including uranophanes and haiweeite [BATES-1992b; BUCK-1993; WRONKIEWICZ-1993]. These phases are generally formed separate from the glass, although they may nucleate on the glass surface, and crystallites may remain suspended in the leachate. A uranium- and titanium-bearing phase (suggested to be brannerite) was also observed to form on SRL 131 glass [ABRAJANO-1990b] and, with thorium, within the altered layer of WVCM 50 glass [EBERT-1991a]; a similar phase was also found suspended in solution [BUCK-1993].

Less is known about the phases affecting the solubilities of Np, Pu, and Am or their incorporation into secondary phases due to the low levels of these elements in glasses used in laboratory tests and limitations of analyzing these elements. In addition, the relatively high solubility of neptunium and the fact that plutonium and americium are preferentially fixed onto metal surfaces results in only small amounts being available for secondary phase formation in leach tests. Plutonium and actinide-bearing phases are typically in very small concentrations and may be sorbed on the altered glass surface or may be suspended in the leachate as colloids. Characterization of plutonium and actinide-bearing phases has been achieved by filtering solutions through holey carbon grids and analyzing the filtrant in an electron microscope [BATES-1992a; CUNNANE-1991a; BUCK-1993]. Microcrystallites of brockite [$(Ca,Th)PO_4 \cdot H_2O$] which have incorporated plutonium and americium have been observed both isolated and supported on colloidal clay particles removed from solution [BATES-1992a]. The similarity between clay colloids removed from solution and clays at the surfaces of reacted glass suggests that material may, under some conditions, exfoliate from the reacted glass surface and become suspended in solution in a mobile state [BATES-1992a].

The chemical similarity of radioelements to nonactive elements will result in the substitution of radioelements into other mineral phases which precipitate out of solution, and minerals may incorporate some radioelements via ion exchange. For example, ^{137}Cs may become incorporated into analcime, a sodium aluminosilicate which commonly forms during glass corrosion [HARKER-1987; VAN ISEGHEM-1988a; EBERT-1991a]. Other zeolites may also incorporate radionuclides. Crystalline lanthanoid phases have been identified to form as solid solutions of powellite ($CaMoO_4$) and cerianite (CeO_2) materials during the reaction of R7T7 glass in salt solutions; these phases may also host Am and Cm [ROTHER-1992].

Incorporation of radioelements into mineral phases or their sorption onto stationary mineral phases may immobilize them, depending on the stability of the host phase. Aging of the mineral phases formed due to glass corrosion will result in thermodynamically more stable phases, which may have a different affinity for radionuclides. Colloid formation may also affect the disposition of radioelements over long time periods. Laboratory tests show that aluminum and iron colloids are formed during glass corrosion [VERNAZ-1990], and that these may sorb radionuclides [SHADE-1984; ITAGAKI-1991; EBERT-1992]. Depending on the colloid size, solution chemistry, groundwater flow and the characteristics of the surrounding geology, these colloids may or may not be transportable, and their transportability may change over time. Colloids which settle out of solution during static leach tests may behave differently under dynamic conditions. Actinide-bearing colloids may be formed by exfoliation of alteration phases from corroded surfaces [BATES-1992a].

2.7.3 Colloids

Colloidal systems are systems in which the component phases are highly dispersed such that the properties are dominated by the interfacial regions. Colloids typically range in size between 1 nm and 1 μm [MYSELS-1959; VAN OLPHEN-1977]. However, others consider particles <10 μm to be colloidal [STUMM-1977]. The surface area of colloids is very large ($\sim 10^3$ m^2/g) for some of the smallest particles, and they readily adsorb metal ions of high ionic charge such as transition metals and actinides [McCARTHY-1989].

2.7.3.1 Formation of Colloids

In aqueous solution, colloids can form if the geochemical gradient, groundwater pH, ion composition, redox potential, or CO_2 partial pressure induce supersaturation with respect to readily precipitable solid phases [McCARTHY-1989; AVOGADRO-1984]. These gradients may result either from waste glass corrosion, corrosion of metals, or natural geochemical processes, including microbiological activity, occurring in the vicinity of the waste glass. For example, schematic diagrams (see Fig. 2-40) for the formation of silica colloids have been produced by Iler [ILER-1979]. In basic solutions, silica colloids grow to give sols of different particle sizes; however, in acidic solutions or in the presence of electrolytes, aggregation may occur to form gel networks (Fig. 2-40). Degradation of backfilling material caused by contact with groundwater may also result in the release of a colloidal clay fraction. Other sources of colloids are the degradation of the surface layers on the glass [BATES-1992a] or naturally occurring colloids in the groundwater.

Groundwater colloids are composed of inorganic and organic molecular constituents, a mixture of both, or microorganisms. They include detritus of weathering mineral products (clay, SiO_2, $CaCO_3$, and FeOOH), hydrolyzed precipitates of mixed metal ions, macromolecular components of dissolved organic carbon (DOC), e.g., humic substances, loaded with metal ions and biocolloids composed of

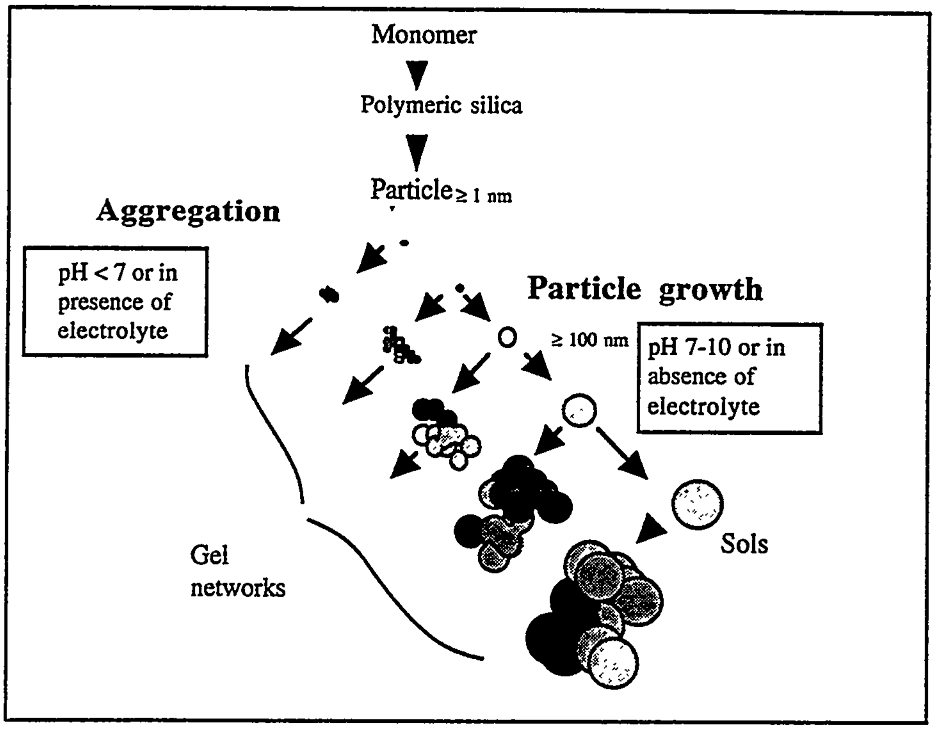

Fig. 2-40. Schematic Illustration of the Polymerization of Monosilicic Acid to Form Seed Particles. In basic solutions, seeds can grow to give sols of different particle sizes (viz. Ostwald ripening), whereas aggregation occurs in acidic solutions or in the presence of electrolytes, which can lead to the formation of three dimensional gel networks (adapted from [ILER-1979]).

microorganisms. Studies have indicated that colloids of inorganic and organic nature are relatively small in size (<450 nm diameter). Choppin describes these types of colloids as being mineral particles covered over all surfaces by a layer of complex organic molecules [CHOPPIN-1992], where the organic part provides the binding sites for sorption of radionuclides.

Radionuclides released from waste glass may participate in the formation of both real colloids and pseudocolloids. Pseudocolloids are formed when radionuclides are adsorbed onto existing colloids, such as those present in natural groundwaters [RAMSEY-1988]. Real colloids are formed from the hydrolysis of highly charged ions in solution. Hydrolysis is followed by polymerization of the metal ions, which leads to the formation of colloids. The rate of hydrolysis depends on the oxidation state of the ion. Actinide ions tend to hydrolyze in the following order: $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$ [KIM-1991b].

Kim [KIM-1991b] has described the formation of actinide real colloids by rapid hydrolysis that leads to high concentrations of Pu and Am hydroxide or oxide in solution. Hydrolysis is a primary step to polynucleation and the eventual generation of actinide real colloids. Tetravalent actinide ions are the most unstable in aqueous solution and readily undergo colloid formation even at low pH values. Formation of such colloids increases the "effective solubility" of actinides such as Pu and Am.

The generation of actinide-bearing colloids can cause the total concentrations of actinides in glass leachates to be orders of magnitude higher than the dissolved concentrations [CUNNANE-1991a; BATES-1992a].

Vernaz et al. [VERNAZ-1992b] has investigated the partitioning of plutonium between colloids and immobile alteration layers in waste glass corrosion. Using the R7T7 glass reacted for one year, they determined that only 1% of the total plutonium was present as colloids, whereas 98% was present in the alteration layer and 0.6% in solution. Studies by Cunnane [CUNNANE-1991a] and Boult [BOULT-1991] support the view that neptunium does not form colloids.

Actinide pseudocolloids are formed by the adsorption of actinides onto a groundwater colloid or any other colloids present. The chemical bond between the adsorbed species and the colloid depends on the chemical and physical state of the ionic species and colloid. For example, Cs^+ and Sr^+ bind by ion exchange and Pb^{2+}, Ac^{3+}, and Th^{4+} by hydrolytic adsorption. Clay minerals, polysilicic acids, and iron hydroxides have been shown to form stable colloids [LEISER-1990]. Americium has been found to adsorb readily onto montmorillonite, which is a common secondary phase formed during waste glass dissolution [OLOFSSON-1985]. The size distribution of actinide pseudocolloids was measured by Avogadro and de Marsily [AVOGADRO-1984]. It was found that very little americium was associated with colloids greater than 200 nm in diameter.

Investigation by Kim [KIM-1991b] has shown the degree of adsorption of Th(IV), Am(III), and Np(V) on alumina to be a function of pH. The results indicate that the generation of pseudocolloids is closely related to the hydrolysis process of each ion of different oxidation states and available surface charge and area of alumina colloids. The adsorption of americium on colloidal quartz and montmorillonite has been examined by Olofsson et al. [OLOFSSON-1985]. In the quartz system more than 50% of the added americium was immediately removed compared to 80-90% for montmorillonite clay.

Organic pseudocolloids such as humic and fulvic acids may be important in some groundwaters. Dearlove et al. [DEARLOVE-1991] found that the colloid concentrations in Gorleben groundwaters were directly proportional to the dissolved organic carbon (DOC) concentration. Trivalent and tetravalent elements (such as rare earth elements, actinides, iron, hafnium, thorium, and zirconium) were associated with organic humic colloids. Most of these colloids ranged in size from 15-1.5 nm. Only 10% of the solution concentration of calcium, barium, and strontium resided in these colloids.

Colloids can be formed by spallation (see Section 3.6 for a further discussion of spalled colloids in dynamic weathering tests) of surface layers from the waste glass (referred to as primary colloids) [BATES-1992a; BUCK-1993] or by nucleation and growth of precipitates in the leachates (referred to as nucleation colloids) [BUCK-1993]. The nucleation colloids were mostly clay smectite types, but other phases were also found. Colloidal U phases, such as weeksite and a U-Ti phase, have been found in MCC-1, PCT, and steam hydration tests at 90°C (Fig. 2-41).

Kawano and Tomita [KAWANO-1993] have also used TEM to study suspended material derived from glass corrosion. Allophane formed initially during the hydrothermal alteration of volcanic (basalt) glass at 200°C under laboratory conditions. Beidellite, identified by XRD and electron diffraction, was found to form thereafter. The Al/Si ratio, determined from TEM/EDS, was used to distinguish between allophane and the smectite phase.

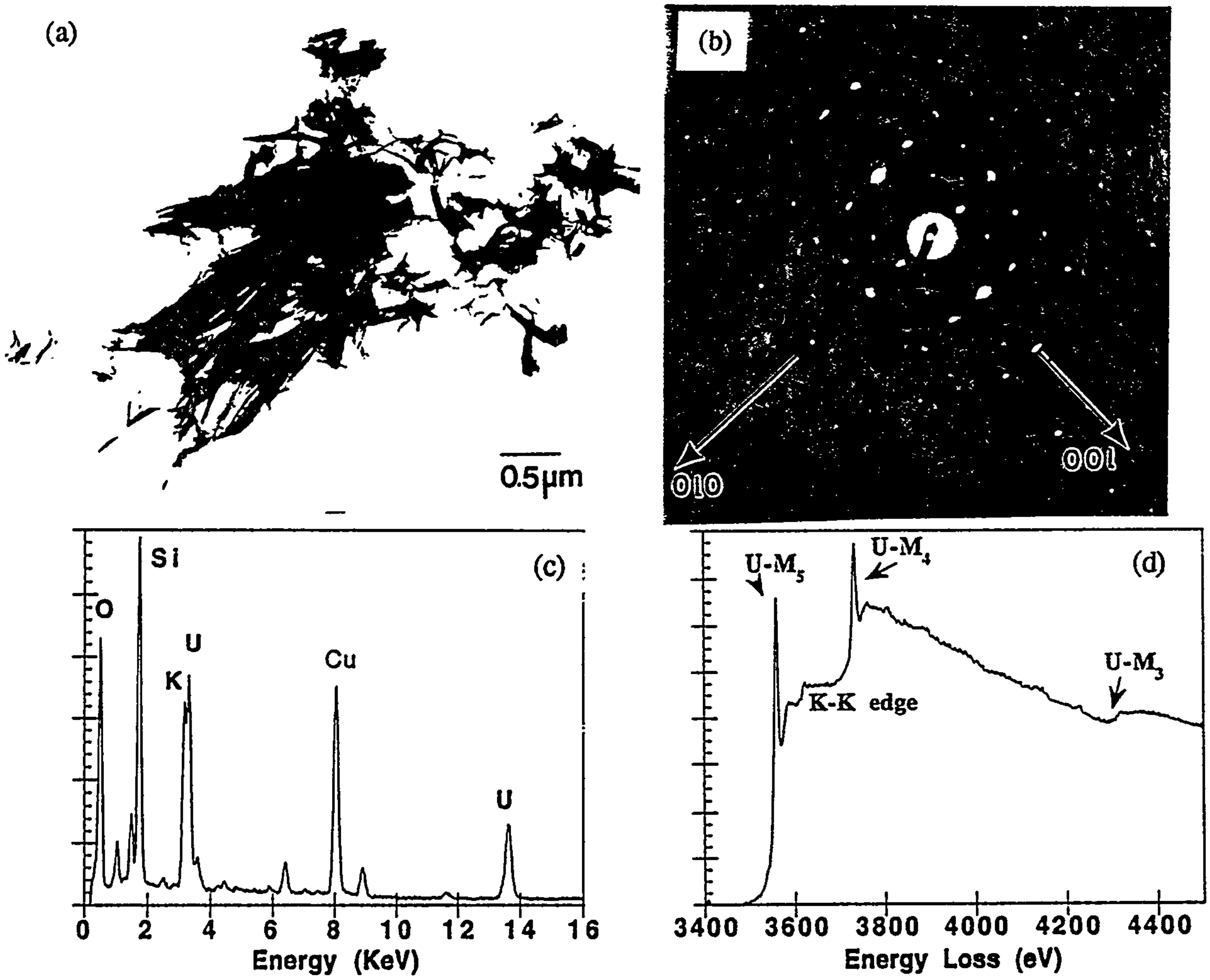

Fig. 2-41. AEM Characterization of Particles from the Leachate of a SRL 131A Glass Reacted under PCT Type Conditions for 560 Days at 2000 m^{-1}: (a) the image of the particles which have agglomerated, (b) selected area electron diffraction (SAED), (c) X-ray spectrum, and (d) electron energy loss spectrum (EELS) (showing M_4 and M_5 uranium edges) (adapted from [BUCK-1993]).

The formation of colloids during the dissolution of waste glass has been described by Ahn et al. in terms of condensation (nucleation within the leachate) and dispersion (spallation of phases into the leachate) processes [AHN-1993]. The evidence for spallation is tentative at present. The supporting data is from TEM characterization of phases present in test solutions.

2.7.3.2 Stability of Colloidal Suspensions

The stability of colloidal suspensions is determined by the interaction of colloidal particles with other mobile or immobile substrates as a result of electrostatic and van der Waals (attractive) forces. These interactions depend on the nature of the colloid and the environmental conditions. The following brief discussion of colloid interactions is intended only to provide a general basis for understanding the few experimental studies that have examined the stability of colloids formed in waste glass corrosion studies.

The surface charge on many colloids, including silicate, alumino-silicate, and oxide colloids, in aqueous solutions depends on pH. As illustrated below, interactions of surface silanol groups with hydroxide and hydrogen ions can lead to positive or negative surface charges depending on the solution pH:

$$\equiv SiOH_2^+ \overset{H^+}{\rightleftharpoons} \equiv SiOH \overset{OH^-}{\rightleftharpoons} \equiv SiO^- + H_2O \tag{32}$$

The pH at which the surface charge is neutral is referred to as the isoelectric point. At other pH values, the surface will be positively or negatively charged. This surface charge is balanced by a counter ion charge distribution in the surrounding solution which is referred to as the electric double layer. This double layer is characterized by a dense layer of counter ions (referred to as the Stern layer) immediately adjacent to the charged surface and a more diffuse outer layer of counter ions (referred to as the Gouy layer). Progressing outward from the surface the electric potential decreases rapidly in the Stern layer and more slowly in the diffuse Gouy layer. As a charged colloidal particle moves in an aqueous solution, a layer of solvent molecules immediately adjacent to the particle surface moves with it. The potential at the shear plane between the mobile and stationary (reference frame associated with the solution) fluid is referred to as the zeta potential.

The zeta potential of a particle determines the electrostatic repulsion between it and similar colloidal particles or immobile substrates. When the zeta potential exceeds the van der Waals attractive force at the shear plane, the coulomb interaction barrier inhibits interactions such as agglomeration. As illustrated in Fig. 2-42, increasing the ionic strength of the solution results in compression of the electric double layer and a corresponding reduction in the zeta potential. The zeta potential in a low ionic strength solution (illustrated by ξ_1 in Fig. 2-42) may greatly exceed the van der Waals attractive potential while, at high ionic strengths, the van der Waals attractive potential may be greater than the zeta potential (illustrated by ξ_3 in Fig. 2-42). This explains why high ionic strength solutions can lead to destabilization (as a result of agglomeration) of colloidal suspensions. This phenomenon is illustrated in Fig. 2-40 [ILER-1979]. Altering the pH of the solution in the presence of an electrolyte can, as illustrated, reduce the surface charge and collapse the double layer resulting in flocculation due to the attractive forces between colloids [VAN OLPHEN-1977].

The stability of colloids formed during waste glass dissolution has been examined by Lee and Clark [LEE-1985] and by Feng et al. [FENG-1993a]. The relationship between zeta potential, colloids, and the surface of the leached glass will govern the stability of the colloids. Feng studied the effect of pH on the stability, as determined by the zeta potential. At pH 6, colloids, identified as smectite clays by TEM, possessed the smallest size distribution. As the pH increased, the particles agglomerated and grew indicating that the colloids were unstable under these conditions. The sparse information that is available suggests that the colloids formed in nuclear waste glass reactions are likely to be unstable with respect to agglomeration. However, additional data are needed.

2.7.4 Summary

- The chemistry of the fluid in contact with the waste form, including the redox state, pH, and available complexants, strongly affects the solubility of multivalent glass components, including the radioelements Tc, U, Np, Pu, and Am.

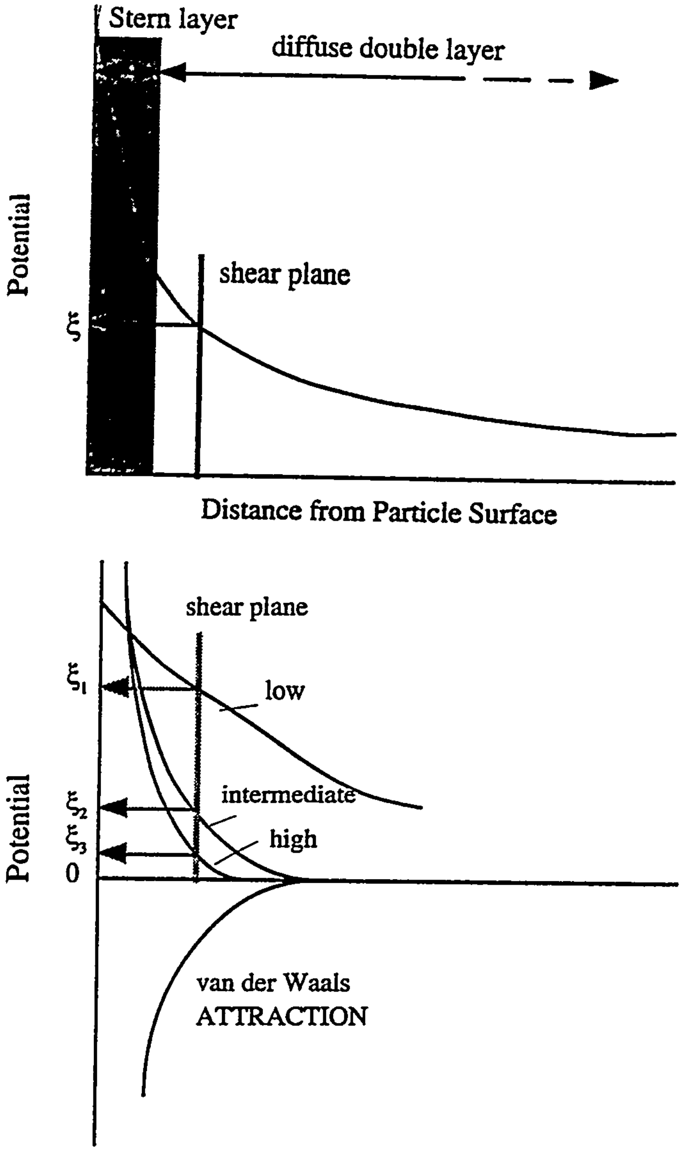

Fig. 2-42.
Schematic of Repulsive and Attractive Potentials for Colloidal Particles at Three Electrolyte Concentrations (adapted from [VAN OLPHEN-1977]).

- The fluid chemistry will be significantly altered due to corrosion of the glass and other materials in the near-field environment. Changes in the Eh, pH, and ionic strength will affect the solubilities and sorptive properties of the radioelements.

- The dominant oxidation states under oxidizing conditions are Tc(VII), U(VI), Np(V), Pu(V), and Am(III), while under reducing conditions Tc(IV), U(IV), Np(IV), Pu(III,IV), and Am(III) are dominant. Other oxidation states may be stabilized by complexation.

- Important complexants include naturally occurring carbonate and humic acids in the groundwater, and may include phosphate, sulfate, and fluoride released from the waste form during corrosion. Complexation may increase or decrease the soluble amounts of radionuclides.

- Important species of actinides in specific valences are expected to be:

    An(III): An^{3+}, AnOH^{2+}, AnCO$_3{}^+$, and organic complexes.
    An(IV): An(OH)$_4$. and organic complexes.
    An(V): AnO$_2$(CO$_3$)$_2{}^{3-}$ and AnO$_2$(CO$_3$)$_3{}^{5-}$.
    An(VI): AnO$_2$(CO$_3$)$_2{}^{2-}$ and AnO$_2$(CO$_3$)$_3{}^{4-}$.

    The sorption energy of the actinides onto mineral surfaces generally decreases as An(III,IV) > An(V) > An(VI). Uranium in the hexavalent state and neptunium in the pentavalent state are poorly sorbed onto most mineral surfaces, while tetravalent plutonium and trivalent americium are strongly adsorbed onto most geologic minerals. Cationic complexes are sorbed much more strongly than are anionic complexes.

- The behavior of uranium is expected to be dominated, under oxidizing conditions, by the chemistry of the uranyl ion, UO$_2{}^{2+}$. It is strongly hydrolyzed and complexed by several ligands which may increase the uranium solubility. Carbonate and phosphate complexes are expected to be present. Reduction to U^{4+} may occur under mildly reducing conditions. U^{4+} is more strongly complexed than UO$_2{}^{2+}$, and is more strongly sorbed by mineral surfaces. Uranium is sparingly soluble under reducing conditions with the species U(OH)$_4$ being the dominant solution species. Uranium is much more soluble under oxidizing conditions, where the species UO$_2$(OH)$_3$(CO$_3$)$^-$ and UO$_2$(CO$_3$)$_3{}^{4-}$ are dominant solution species at basic pH values.

- The behavior of neptunium is expected to be controlled by the chemistry of pentavalent plutonyl as NpO$_2{}^+$ under mildly oxidizing conditions or Np(OH)$_4$ under mildly reducing conditions. Neptunium(V) as NpO$^+$ is more soluble and less strongly hydrolyzed and complexed than Np(IV); NpO$_2$(CO$_3$)$_3{}^{5-}$ and NpO$_2$(CO$_3$)$_2{}^{3-}$ become important above about pH 8 in oxidizing solutions.

- The behavior of plutonium may be controlled by the chemistry of Pu^{4+}, PuO$_2{}^+$, or PuO$_2{}^{2+}$ depending on the redox potential of the solution. Under slightly reducing conditions where Pu(IV,V) dominate, important species will include Pu(OH)$_4$ or PuO$_2$(CO$_3$)$_3{}^{5-}$ and PuO$_2$(CO$_3$)$_2{}^{3-}$ at high carbonate contents. Higher solubilities are expected at pH values above about 9 where the PuO$_2$(CO$_3$)$_3{}^{5-}$ species dominates the solution.

- The behavior of americium is expected to be controlled by the chemistry of the trivalent Am^{3+} species. The Am(OH)$^{2+}$ and AmCO$_3{}^+$ species and organic complexes are expected to be important.

- The behavior of technetium is expected to be dominated by the chemistry of the highly soluble pertechnetate ion, TcO$_4{}^-$, which is not hydrolyzed, complexed, or sorbed onto mineral surfaces. Tc(IV) species may dominate under reducing conditions. The behavior of Tc(IV) species is very different from Tc(VII), and Tc(IV) may become complexed and strongly sorbed onto mineral surfaces.

- The behavior of radionuclides observed in integrated leach tests is consistent with their general chemistry, although the phases controlling their solubilities are not well-known. The total solubilities of Pu and Am are typically quite low under basic solution conditions, and the solubility limits are likely to be exceeded in most glass corrosion tests. The solubility limits of U and Np are several orders of magnitude higher than those of Pu and Am. Technetium is highly soluble under oxidizing conditions.

- A large fraction of released radionuclides may become immobilized upon incorporation into or sorption onto mineral phases present naturally or generated by corrosion of the glass and other repository materials. The alteration layers formed on the glasses typically account for the retention of about 90% of neptunium, 97% of plutonium, and 99% of americium as the glass corrodes.

- Sorption of radionuclides onto colloids present in the groundwater and those generated during glass corrosion will strongly affect the distribution of actinides. Sorption onto colloids may mobilize radionuclides in excess of their solubilities. Sorption is specific to the host mineral phase and the oxidation state of the radionuclide. Sorption of lower oxidation states is generally stronger than that of higher oxidation states.

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3.0 WASTE GLASS WEATHERING

Unsaturated hydrologic conditions are described in Volume I, Section 2.2.3. The following glass/water contact scenarios are possible in an unsaturated repository:

1. Water vapor contact and the associated formation of surface water films on the glass;
2. Periodic dripping of water onto the glass and trickling through the breached waste; and
3. Slow filling of the canister void volume.

The key difference between these scenarios and the glass aqueous corrosion conditions discussed in Section 2 is the limited volume of water available for reaction. Although the engineered design will severely limit the ingress of water [LUTZE-1988b; SCP-1988], it is rare that conditions that involved limited water contact are utilized in waste glass testing [BATES-1984a, -1990b; SEITZ-1984a; RYERSON-1992]. The conservative bounding condition for studying glass corrosion occurs at infinite dilution, where the forward rate of reaction is obtained. This forward rate is believed to be the fastest rate at which the glass can react. Thus, standard tests to evaluate glass performance--e.g., Soxhlet, flow-through, MCC-1, or MCC-3/PCT--initiate the corrosion with a relatively large volume of water; however, in actuality, glass/water contact will be limited by ingress of water through the canister, and the initial reaction is likely to take place with a small volume of water. Tests done with small volumes of water are described as unsaturated in this chapter and are designed to investigate whether actual water contact modes affect glass reaction. A predictive model should be developed on the basis of a variety of tests that initially identify important processes and conditions, identify the parameters to be included in modeling, and develop and validate the model with regard to service conditions [ASTM-1991].

The alteration of HLW glass under saturated conditions has been studied extensively, but relatively few studies have evaluated unsaturated conditions. In this section, weathering (see glossary) is used as a general term to describe the corrosion process that occurs under unsaturated conditions. Following the description provided by Clark [CLARK-1979], weathering includes corrosion under both static and dynamic conditions. The weathering occurs by the glass corrosion processes identified in Table 1-1 and, thus, is a special case of glass corrosion. Many standardized test methods have been established to evaluate glass leaching, but no standardized tests are available to study HLW glass weathering.

Because of the limited amount of information regarding HLW glass weathering and the need to evaluate effective test methods, information related to the weathering of glass types other than HLW glass has been reviewed. Glass corrosion under unsaturated conditions has been studied by the commercial glass industry in evaluating the durability of glassware, window panes, and optical glass and has generally been referred to as weathering. Glass weathering has also been studied by conservators interested in preserving medieval stained glass windows, by archaeologists and geologists who have studied the reaction of natural glasses, and by nuclear scientists evaluating the long-term disposal of waste glass. Although there is overlap between information and techniques used in each of these disciplines, it is instructive to review the literature according to these groupings while recognizing that the range of glass compositions varies greatly and is significantly different from HLW glass.

The literature reviews of commercial, historical, and natural glass focus mainly on vapor contact; these studies together with studies done on waste glass provide a general description of the corrosion process. Studies of dripping water and slow filling of a canister void are addressed mainly through studies on waste glass, including both glass corrosion processes and radionuclide release. Information on the weathering of natural and historical glasses is briefly described in this section in the context of the reactions shown in Table 1-1 and the associated physical processes.

3.1 Commercial Glasses

The weathering of commercial glasses such as those used for containers, windows, optics, and data transmission is a serious issue that affects product utility. These glasses span a range of compositions (see Table 3-1), and considerable testing has been done under typical service conditions, including exposure to humid air or intermittent condensation. The majority of studies have focused on soda-lime-silicate (NCS) or alkali-borosilicate (ABS) glasses. Two general interaction modes between glass and humid air have been identified as (1) static weathering, where water sorbs onto the surface in thin films where it reacts with the glass and (2) dynamic weathering, where water vapor contacts, condenses, or sorbs to the glass surface; accumulates; and eventually runs off the surface. These water interaction modes are similar to those identified for HLW glasses in unsaturated host rock repositories (Volume I, Section 2.2.3).

Most of the early studies on weathering concentrated on the development of test methods combined with qualitative descriptions of the reacted glass. The description of test results focused on performance of the product for a particular application, not necessarily on the extent of reaction. The results are more descriptive than mechanistically based and appear qualitative compared with recent work on glass corrosion. However, these test results form the basis for identifying important variables that affect glass weathering. Later, after the effects of environmental parameters on test results were better understood, more effort was devoted to accelerating the overall reaction process and elucidating the reaction process [NEWTON-1985b; ELSDEN-1919; STOCKDALE-1950; DIMBLEBY-1939].

Table 3-1. General Composition of Commercial Glasses

Type	Principal Use	Major Constituents[a]
Soda lime silicate (NCS)	Bottles, windows	R_2O-RO-SiO_2
Alkali borosilicate (ABS)	Optical, general, cooking ware	R_2O-B_2O_3-SiO
Hard crown (BC)	Optical	R_2O-RO-SiO_2
High silica (HS)	High temperature	SiO_2
Dense barium crown (DBC)	Optical	BaO-B_2O_3-SiO_2
Light flint (LF)	Optical, decorative	SiO_2-R_2O-PbO

[a] R_2 = alkali element, R = alkaline earth element.

Early weathering tests exposed NCS glass to humid air for a set period of time and noted, for example, that within 24 hours at 80°C there was distinct dimming of the surface [NEWTON-1985b]. Although the extent of glass reaction was mainly a subjective judgment, it was determined that the extent of weathering was a function of temperature, time, relative humidity, and glass composition [OWENS-1942]. Simpson "quantified" the process somewhat with the development of a haze test in which the extent of weathering was measured by a photocell as a function of time [SIMPSON-1951, -1953, -1958, -1959]. In Simpson's terms, the less light transmitted through the glass, the more the glass was weathered, but no absolute measure of glass reaction was determined. He found that NCS and ABS glasses reacted to form haze in a static weathering environment where the temperature was cycled between 48 and 58°C over a two-hour period and the relative humidity was kept constant at 100%. When he tried a constant temperature-humidity environment, too much condensation formed and rinsed away the haze. During further application of his method, Simpson concluded that the haze was due to either surface roughness or salts that formed as the elements released from the glass reacted with acidic gases in the atmosphere, e.g., CO_2, SO_2 [SIMPSON-1958]. Simpson also noted that glasses previously exposed to reactive environments (humid storage or complete liquid submersion) such that they were preleached, developed a haze four times faster than pristine glass [SIMPSON-1953]. Figure 3-1 illustrates phases formed on the glass surfaces due to static weathering.

Moser [MOSER-1961] used the Simpson approach of cyclic temperature and constant relative humidity to study the weathering of NCS glass. He studied the scumming and staining of glass with SEM and concluded that scumming was a gradual buildup of crystalline material containing Si, Na, Ca, Mg, Fe, and $Al_2O_3 \cdot SiO_2$ in the glass surface (Mg, Fe, and Al are minor components in the glass). During the scumming process, flaking and cracking of the glass surface was very pronounced. Etching or the formation of a reacted surface layer was referred to as staining. Cracking and spalling were also reported by Shelby [SHELBY-1980b] in the static weathering of an Fe-rich glass exposed to about 100% relative humidity and temperatures of between 50 and 70°C. He followed the reaction with SEM and RNRA and suggested that the spallation was due to an alkali-depleted layer that became stressed, spalled off, and exposed new surfaces for continued reaction. Both Moser and Shelby noted that scumming occurred when moisture collected at random sites and eventually formed a film over the entire surface and that the surface was marked by pits or precipitated siliceous material.

Static weathering was also produced without runoff by using a carefully controlled humidity chamber to examine NCS and ABS glasses [STOCKDALE-1950]. In these tests, salt solutions were used to control the humidity at 90°C, and the reacted samples were covered by a uniform film of moisture. The effects of 95, 73, and 57% relative humidity were evaluated, with the weathering effect being in a ratio of 54:15:1 on the basis of percent change in light transmission. The NCS glasses weathered much more rapidly than the ABS glasses.

An extensive set of weathering tests has been reported by Walters and Adams [WALTERS-1975], who evaluated the performance of 26 glass compositions under static and cyclic temperature conditions. The static tests were done at varying relative humidities and 50°C, whereas the cyclic tests were conducted at varying temperatures following Simpson's procedure. In each case, the tests were done to prevent runoff. Several different methods, including alkali-release measurement and SEM, were evaluated to assess weathering, but visual observation of the surface alteration was chosen as the best comparative measurement. The static tests indicated that weathering effects can be observed down to 30% relative humidity with, in some cases, the extent being similar to that observed at 90% and that weathering can occur without the release of alkali. Compared with the cyclic tests, the static conditions always produced a greater extent of reaction and, if the glass surfaces were

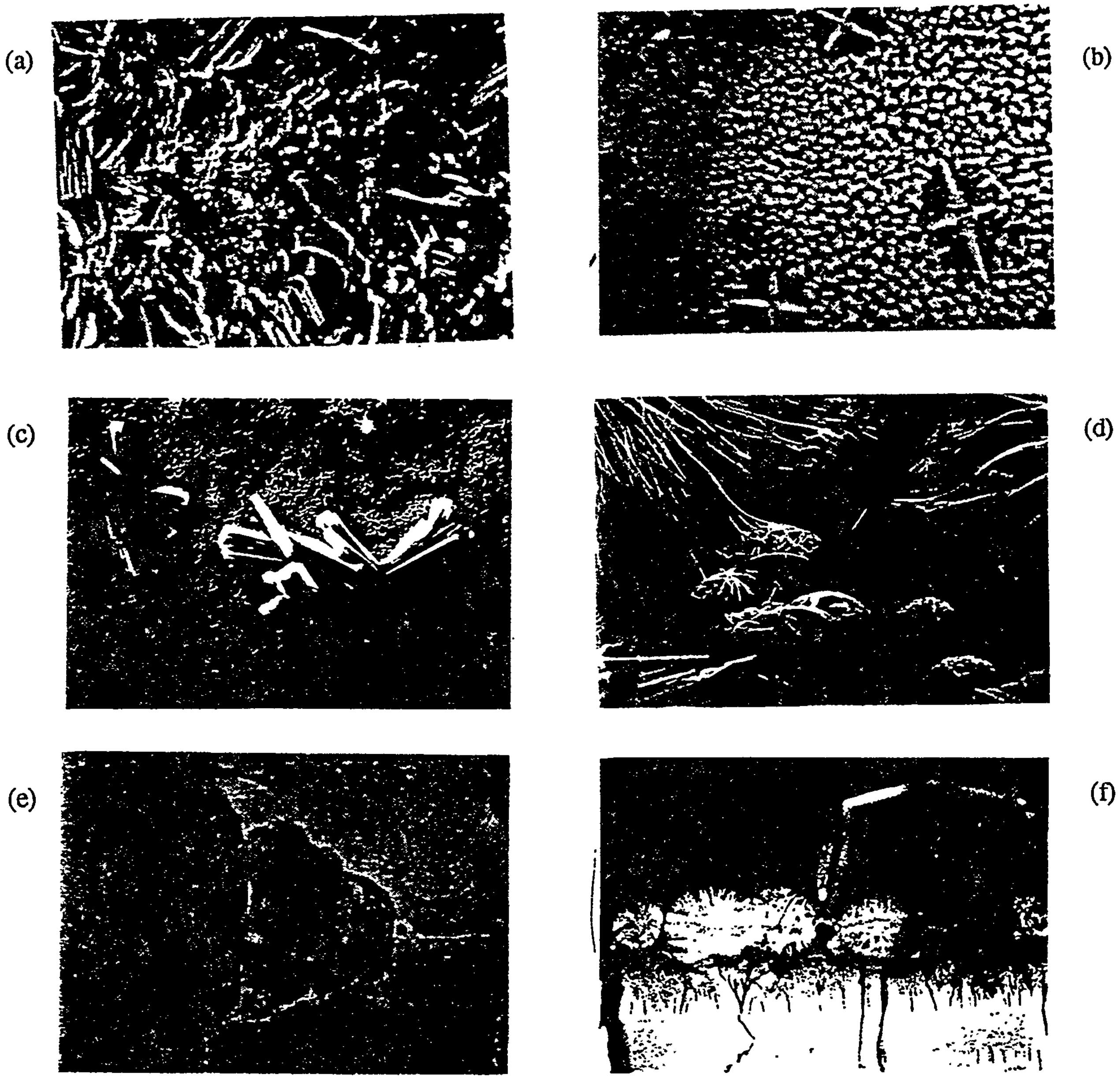

Fig. 3-1. Micrographs of Weathered Glass Surfaces (a) Naturally Weathered Medieval Window Glass (adapted from [SCHREINER-1988]), (b) NCS Glass Weathered in a Humidity Cell at Temperatures Cycled between 48° and 58°C (adapted from [MOSER-1961]), (c) Natural Basalt Glass Weathered at 240°C (adapted from [BYERS-1987]), and (d) SRL 211 HLW Glass Weathered at 240°C (adapted from [BATES-1982a]). Cross sections of weathered glass are shown in (e) a medieval glass buried in calcareous soil for 288 years (adapted from [NEWTON-1971]) and (f) basalt glass weathered at 240° (adapted from [BYERS-1987]).

periodically rinsed with water, the extent of weathering was drastically reduced because the reaction products causing the observed weathering were washed away. The ABS glasses produced fewer reaction products and performed much better than the NCS glasses under both types of tests.

Clark et al. [CLARK-1979, -1983] have put much of the early static weathering work at temperatures below 100°C into perspective for HLW management. For either NCS or ABS glass, the initial reaction process is an alkali-hydrogen ion exchange. The extent to which the glass weathers depends on the fate of alkali ions once released from the glass structure. If the alkali ions are released from the NBO sites in the glass and occupy sites previously filled by hydrogen ions (either on the surface or in the glass), then, once the available sites are saturated, the reaction must stop and the glasses will appear unweathered. If the alkali reacts with gases such as CO_2, Cl_2, or SO_2 to form crystalline phases, then the reaction can continue and the glass will appear weathered. The precipitates act as an alkali sink, and continued weathering can lead to hydrolysis of the glass and subsequent cracking and spalling (see Section 2.1.2). Qualitatively, these results show that in contact with water vapor, glass reacts in a way that alters its structure, affects its subsequent durability when contacted with liquid water, and even results in the release of material from the glass.

Further release occurs if the glass surface is rinsed with liquid water. During the development of tests to study the static weathering of glass, it was found that conditions had to be carefully controlled or water would condense and run off the glass surface. During the rinsing process, the reaction products that initially formed during weathering dissolved and the surface of the glass actually improved when measured for haze or percent transmittance (although, presumably, the glass continued to react). The same observations have been made for medieval glasses and, thus, most experimental work has avoided the rinsing process.

To evaluate the effects of dynamic weathering, studies have been done with binary and commercial glasses at temperatures between 23 and 100°C [SANDERS-1973a]. At 23°C and 100% relative humidity with a binary glass, the glass reacted to yield a dealkalized layer, but restructuring of the reacted layer was inhibited until runoff occurred to remove the alkali from the gel. When this occurred, the remaining silicic acid in the gel condensed and the extent of reaction increased rapidly, such that after 14 days the extent of reaction due to dynamic weathering was the same as that which occurs in leaching tests. These data are illustrated in Fig. 3-2a and are compared to other conditions for which the glass corrosion rate has been observed to increase after a period of time. Compared with the other examples shown in Fig. 3-2, the data of Sanders are unique in that the rate change occurred at ambient temperature. However, it is important to note that static weathering tests done at temperatures above 100°C (e.g., Fig. 3-2c for WVCM glass) are done at pressures greater than 0.1 MPa (1 bar) and relative humidities of 100%. Such conditions will not occur in an unsaturated repository. In an unsaturated repository, the maximum pressure is 0.1 MPa. Thus, if glass were exposed to water vapor at 200°C in an unsaturated repository environment, the relative humidity of water vapor would be very low, and little reaction of the glass would be expected. The tests for which the results are shown in Fig. 3-2c and 3-2d were intended to observe corrosion phenomena under accelerated aqueous corrosion and weathering conditions which allow examination of the phases formed at high values of the reaction progress parameters.

To further examine the importance of rinsing the leached material from the surface, tests with a more complex ABS glass were performed [CLARK-1983]. Sodium depletion from the glass was observed to be more rapid for dynamic weathering than static leaching, which can be explained by the high Na^+ concentration gradient that was maintained due to runoff. Calcium was also depleted during dynamic weathering but remained on the surface during static weathering and leaching.

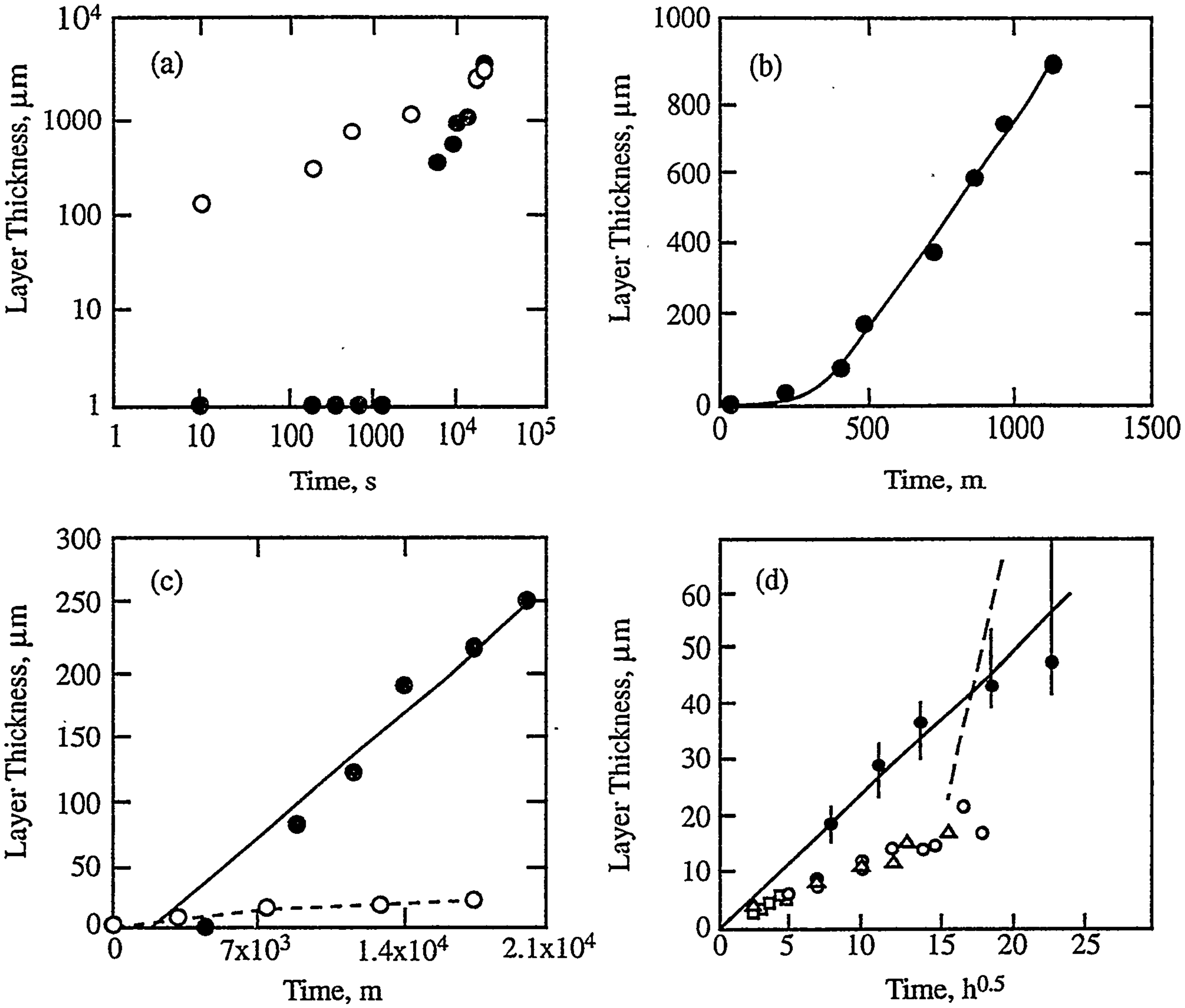

Fig. 3-2. Extent of Static Weathering for Various Glass Types Illustrated by Plotting Reacted Layer Depth vs. Time for (a) Binary LiSi Glass Reacted at 23°C, (○) Represents Glass Leached in Liquid and (•) Glass Exposed to Static Weathering. The extent of weathering was measured using infrared spectroscopy and the extent of condensation of SiO bands was monitored (adapted from [SANDERS-1973a]); (b) NCS glass reacted at 200°C, (•) glass exposed to static weathering at 200°C, (○) glass exposed to liquid water at 200°C (adapted from [CHARLES-1959]); (c) WVCM glass reacted at 200°C, (•) static weathering, (○) liquid water (adapted from [EBERT-1991a]); (d) SRL 131 glass reacted at 202°C, (•) liquid water, (○,Δ) duplicate static weathering initial reaction stage, (---) second reaction stage (adapted from [ABRAJANO-1989]). In each example, the initial extent of weathering was found to be less than that for reactions in liquid water. After extended reactions, the extent of weathering either equaled (a) or exceeded that observed for reactions in liquid water. The weathering process consists of a slow initial stage followed by a more rapid second stage. In the slow stage, the rate is slow due to the buildup of reaction products. In the rapid stage, these reaction products are removed from solution and the rate of reaction increases.

The weathering tests described above were done at temperatures below 100°C and indicate that some breakdown of glass structure can occur under unsaturated conditions. However, to accelerate glass corrosion to better evaluate the reaction processes, several studies have been done with NCS and ABS glasses at temperatures between 100 and 300°C. These studies are particularly interesting because they provide insight into long-term vapor interactions that are likely to occur in an unsaturated environment. At temperatures above 100°C, two different corrosion processes are observed for nearly identical glass compositions. Charles [CHARLES-1959] tested NCS glass in saturated conditions (100% relative humidity) and dry steam (90% relative humidity) at temperatures between 175 and 250°C in a manner to fully avoid condensation and runoff. He observed an increase in the corrosion rate after about 400 min (Fig. 3-2b) and the formation of a thick corrosion rim (reacted layer) on the glass, which makes a sharp boundary or interface with the glass. Similar behavior was observed under both test conditions, but in dry steam the onset of the rate increase took longer to occur. Charles described the reaction process as occurring in two steps. The first step involved the release of Na ions from the glass structure in conjunction with the production of hydroxyl within the layer. This increased the "pH" in the layer and resulted in an autocatalytic hydrolysis (second step) of the glass network and acceleration of the reaction rate. In fact, the longer-term reaction in steam was observed to be faster than corrosion in liquid water because of the slower pH buildup that occurs in liquid. On the basis of the temperature dependence of the reaction, an activation energy for the initial stage of the reaction was calculated to be about 80 kJ/mol, which was attributed to diffusion-controlled ion exchange [ABRAJANO-1989]. When the results of Charles (Fig. 3-2b) are compared with data obtained on a HLW glass (Fig. 3-2c), the curve profiles and reported activation energies are similar for both glass types. Thus, similar processes may be occurring for both glasses, although the importance of individual processes (Table 1-1) may be different for each glass type.

The observation of a rate increase during exposure to humid air is not ubiquitous. Bartholomew et al. [BARTHOLOMEW-1980] exposed a silica-rich (78 wt.%) glass to saturated and dry steam at temperatures above 100°C and, although a diffusion-controlled process was observed--as determined by the $t^{1/2}$ functionality of layer thickness growth--no rate increase occurred. However, the test conditions were such that runoff from the glass surface must have occurred, as evidenced by a pH increase in the humidity-controlling water bath. This runoff would impact the formation of precipitates, which have been related to increased reaction rate (see discussion below).

Studies done under conditions that suppress precipitate formation have resulted in water diffusing into the glass without alkali release. Specifically, Moriya and Nogami [MORIYA-1980] have reported results in which there was runoff from the surface, and Tomozawa and Molinelli [TOMOZAWA-1984] did experiments in a nitrogen water-vapor atmosphere. In both cases, water diffusion was identified as the dominant reaction process. Tomozawa and Tomozawa extended this work in a later study [TOMOZAWA-1989] on an ABS glass in which the glass was reacted in air-based saturated and dry steam environments. The glass hydration was monitored with infrared spectroscopy and the surface was examined for precipitates. The investigators observed no precipitate formation and concluded that, because alkali cannot escape from the glass, surface water should simply diffuse into the glass. They measured an activation energy of about 52 kJ/mol, which is less than that observed for ion exchange.

The results of higher temperatures reinforce the previous discussion of Clark et al. [CLARK-1979] in that the formation of crystalline phases on the glass surface can influence the dominant process by which the glass corrodes (diffusion vs. ion exchange and hydrolysis) and the type of layers that are formed (water-containing glass vs. reacted layers). The nature of the reacted layers or altered glass can ultimately affect how radionuclides are released during the corrosion process.

Thus, if hydrolysis has occurred, radionuclides may be released by spallation, dissolution, or secondary phase formation. However, if the glass structure is maintained, as with water diffusion, the radionuclides will be retained as part of the glass structure.

As the test methods and analytical equipment developed over time, a fairly consistent picture emerged for the weathering of a wide range of commercial glasses. The first step in either dynamic or static weathering is the release of alkali from the glass. If alkali release can proceed, either by the incorporation of released alkali into precipitated phases or by their being rinsed from the surface, the alkali depletion process can continue and the rate of corrosion may increase. Concurrent with alkali depletion, hydrolysis reactions may occur (see Table 1-1), and a surface layer can form that tends to exfoliate from the glass. The reaction process can then continue and repeat the corrosion cycle. Under conditions designed to evaluate long-term reaction (increased reaction rate due to either less-durable glass compositions or elevated temperatures), an increase in the corrosion rate has been observed after a period of time. If there is no process to remove alkali from the surface, then the ion-exchange reaction is halted but water diffusion into the glass continues. In this case, the glass structure remains intact, but the water content of the glass is increased. The processes and reactions used to interpret weathering are similar to those discussed for glass leaching and, in many respects, it is instructive to interpret weathering as a very high S/V leaching condition.

3.2 Historical Glasses

Historical glasses, including medieval window glass and ancient glass dating from as early as 2,000 B.C., can be used to evaluate the glass reaction under weathering conditions. Additionally, conservators are conducting laboratory weathering experiments to better understand factors that affect the durability of these glasses so that better methods of glass preservation can be developed. In general, the composition of historical glasses falls within the NCS classification with K sometimes being the dominant alkali component.

In research on preservation of glass-based materials, one goal has been to relate the interaction between the environment and the materials through understanding the processes by which the materials degrade. Thus, by identifying important physical parameters that affect corrosion, better methods to preserve materials can be developed. During the past century, there has been concern over the continued degradation of stained glass windows under exposure to conditions similar to commercial glasses or waste glass stored in an unsaturated environment. (For reviews, see NEWTON-1975, -1982, -1985b; FRANK-1982.) These conditions include exposure to humid air, intermittent water contact, and burial in unsaturated soil where the relevant environmental parameters include relative humidity; the extent of precipitation, condensation and runoff; temperature and associated gradients; reactive gases in the air; and the effects of soil alkalinity and groundwater contact. Additionally, the effect of glass composition on the extent and nature of corrosion is also a major factor. Because of the large number of potentially synergistic effects and the fairly qualitative approach used to describe the alteration effects, only recently has a better understanding of the corrosion processes for historical glasses emerged.

The weathering of historical glasses can be described in terms of static and dynamic weathering, and the burial in unsaturated soil can be considered an extension of static weathering, i.e., the corrosion products are not washed away from the glass. The types of weathered surfaces have been classified generally as unweathered, pitted, crusted, fractured, and combinations of these. Crusted glass (glass with an attached reacted layer) has received considerable attention because it is the cause of the iridescence found on museum pieces as well as the laminated alteration on buried artifacts.

Medieval glass compositions depend on the source of natural constituents used to make the glass but generally fall in the NCS classification and have an "SiO_2":RO:R_2O mole ratio of 55-70:15-25:15:25 where "SiO_2" represents the network formers, mainly SiO_2 but also small amounts of Al_2O_3, Fe_2O_3, P_2O_5, TiO_2, PbO, and so forth; RO are the divalent network modifiers consisting of lime (CaO) and magnesia (MgO); and R_2O are the alkali network modifiers, mainly soda (Na_2O), potash (K_2O), and small amounts of MnO, CoO, CuO, or ZnO [NEWTON-1985a; COX-1979].

Surface layers have been found on ancient glasses after burial in damp soil or after exposure to humid air in the laboratory or in natural settings. Under burial conditions, the crusts have formed as discrete bands or layers [BRILL-1961a, -1961b, -1963]. It has been proposed that the number of layers can be related to the length of time the object was buried and that the layers are formed due to cyclic variation in temperature or water available for reaction, similar to the formation of Liesegang rings (laminar structures found in naturally weathered minerals). Under the first hypothesis, it is proposed that, during the wet season, the water penetrates into the glass and leaches out alkali and alkaline earth ions; subsequently, the remaining silicate structure becomes partially hydrolyzed. During the dry season, the water evaporates and the silica condensation reactions occur (Table 1-1), resulting in the formation of physically separate layers. The process is repeated yearly, resulting in a relatively linear rate of alteration in which the rate of glass corrosion under ambient conditions is about 4 to 8 µm/yr [BRILL-1961a; NEWTON-1985a; RAW-1955; SHAW-1965]. Examples of intact laminated crusts that correspond well to the known age of the sample have been noted for medieval glass reacted for 400 to 800 years and Roman and Islamic glasses reacted for 900 and about 1500 years [BRILL-1961b]. The crusts have been found to be either quite fragile (spall from the glass) or adherent. The dating method depends, of course, on the entire layer structure being intact.

An alternative method proposed for the formation of layers is in-situ segregation and redistribution of elements from the glass as the corrosion (network-hydrolysis) process occurs. This hypothesis is based on a comparison with Liesegang rings formed in natural samples, but it has not been confirmed by any high-resolution technical investigation of the layer structure for historical glasses. Studies of HLW glasses also show layering, and high-resolution examination of the structure of these layers suggests the segregation process is the cause of the layering [ABRAJANO-1990b]. Early work on characterizing the structure of the layers [RAW-1955; SHAW-1965] was limited by the technology at hand, and the results offered only tempting insight into the reaction process. Raw [RAW-1955] examined a crusted glass (about 50% SiO_2, 20% CaO, and 12% K_2O) that still had "unaltered" glass in the center. The crust was layered and highly porous; it consisted mainly of Si, Ca, Al, and H_2O; was depleted in alkalis, Ca, and Mg; and was enriched in Ti, Al, Fe, and Si, with Fe and Mn (presumably from the soil) on the surface. An interesting aspect of the "unaltered" glass was that it contained about 5% H_2O, which suggests that water diffusion, without breakup of the glass network, may be a precursor to layer formation.

Shaw [SHAW-1965] examined heavily altered layers formed during 800 years of burial. He noted a clear variation in the Si and Ca content of the layers, with a repetitive variation that agreed with the number of layers; a boundary of Al, P, and Ca parallel to the layers; and an enrichment of Mn in segregated regions of the crust. He reported the crust to be crystalline but did not identify the phases. The observation of segregated P, Ca, and Mn has parallels in reactions observed for HLW glasses in which these elements have segregated to form stable secondary phases [ABRAJANO-1990b; BATES-1991c, -1992c].

The importance of the structure of the crusts and accompanying layers is the insight they provide into how the glass reacts under unsaturated burial conditions. One problem with the relationship between the number of layers and the age of the sample is that multiple layers are also formed when glass is exposed to humid air in controlled laboratory experiments [RAW-1955] or submerged in sea water [NEWTON-1971]. Raw [RAW-1955] performed an autoclave experiment in CO_2-free steam at 144°C and 4 atm for 4 hours, using a (SiO_2 68%, CaO 6%, Na_2O 24%, Al_2O_3 1 wt.%) glass. He produced a crust with 10 layers that exfoliated during reaction, and he suggested that the layers were formed in situ as the glass reacted. Within the context of the processes described in Table 1-1, Raw suggested that as network hydrolysis occurred, the elements redistributed to form layers without dissolving in the bulk solution.

Recently, controlled-atmosphere experiments have been done at lower temperatures (-20 to 40°C) with the relative humidity uniformly cycled daily between 30 and 100% [SCHMIDT-1991]. The purpose was to develop a test method that could be used in the field to examine static and dynamic weathering effects in situ and to examine the effects of pollutant gases on glass alteration. The rate of the reaction processes was purposely increased by choosing glass compositions of known poor durability (48 to 60 wt.% SiO_2, 15 to 29% R_2O, and 17-25% RO). The thickness of the reaction layer and elemental composition were measured with SEM, and the structure of the layer was probed with infrared spectroscopy. The investigators did not identify a layered structure but found that, in the static humid air environment, a syngenite/gypsum crust formed that was preserved and produced an extent of reaction, as measured by layer thickness, similar to that noted for dynamic conditions in which the crystallites were rinsed away. The extent of alkali depletion was assisted by the formation of microcracks in the leached layer and crystallites on the surface. An SEM image indicated a total penetration of about 6 μm due to crack formation and a layer thickness of about 2 μm after about one year. In these tests, the test duration was probably not long enough for multiple layer formation.

Alteration of glass exposed to humid air of varying relative humidity was examined by Schreiner et al. [SCHREINER-1986, -1988] using SIMS and SEM. Two glasses were examined, one that produced thick laminated layers (SiO_2 40 to 50 wt.%, K_2O 15 to 20%, CuO 15 to 25%), and one apparently unaffected by long-term exposure (K_2O-CaO-SiO_2 samples with 15 to 30 wt.% PbO). Although a complete description of the layers was not provided, the outermost layer was described as consisting of elements leached from the glass and components of the atmosphere. For the Pb-containing glass, a Pb-rich surface layer was observed that inhibited further corrosion. A beneficial effect of Pb on glass reaction has also been noted in leaching experiments of HLW glasses.

A current description of at least the initial processes that occur during the static weathering of medieval glass is given by Schmidt and Fuchs [SCHMIDT-1991] and Fuchs et al. [FUCHS-1991]. The description is similar to that used by Charles [CHARLES-1959] where ion exchange, prior to crystallite formation, occurs at an initial $t^{1/2}$ rate. If CO_2 is present, sodium or potassium carbonate will be formed on the surface. If enough K is present in the glass, Ca will also be released from the glass structure. The leaching of Ca is also enhanced by the presence of SO_2, due to the formation of insoluble syngenite, which leads to an increase in the driving force for the reaction because there is a "sink" for the Ca. As this process occurs, an alkaline-free, silica-rich gel surface layer is formed. However, due to condensation of $\equiv$SiOH groups within the gel, stresses are established that result in cracking and exfoliation. A description of the process leading to multiple layer formation and the long-term static weathering of the glasses is discussed in Section 3.4.

Not all ancient glasses exposed to static weathering conditions are obviously altered. The good durability of some examples of well-preserved Roman glasses has been attributed to burial under arid desert conditions and the high Na (vs. K) content in Roman glasses compared with medieval glasses [NEWTON-1985b]. Several particularly interesting examples of medieval glasses that are apparently unaltered are also known. Cox [COX-1979] has catalogued the appearance vs. composition of glasses from York Minster and found that glasses with a silica content of about 70 mol.% with alkali (mainly Na rather than K) have shiny surfaces that appear unaltered. For example, glass #271 has a SiO_2:R_2O:RO mole ratio of about 73:17:10, a composition that is very similar to the commercial glass reacted by Moriya [MORIYA-1980] under accelerated static weathering conditions. By extrapolating Moriya's results on the basis of the time-temperature relationship presented, the glass should hydrate at a rate of about 1.6 μm/100 yr at 20°C. Although it is not clear from Moriya's description as to what type of reacted layer formed on the glass (crust or water diffusion with no breakdown of the structure), he described the corrosion process in terms of water diffusion and made no reference to crystalline phases. Thus, it is possible that the "unaltered" York Minster glass had hydrated by water diffusion but with no structural breakdown.

Newton [NEWTON-1969] also has examined two glasses with very similar compositions that were buried for about 450 years in damp soil. The mole ratio for the glasses is "SiO_2":RO:R_2O = 62-67:22:14, with the only significant difference being in the total "SiO_2" components. The glass with the higher "SiO_2" content is unweathered whereas the other forms a thick crust. Newton tried to resolve this difference by examining the reaction of the unweathered glass in the laboratory using a crushed glass leach test at 100°C for 1 hour. He noted little difference in the glass reaction between the two glasses. However, the problem was studied further by El-Shamy [EL-SHAMY-1973], who performed leach tests with crushed glass at 60°C for 1 and 72 hours. In this experiment, the glass durability changed markedly when the "SiO_2" mol.% fell below 67%. El-Shamy reasoned that, below 67 mol.%, there is an interconnecting pathway that allows direct diffusion of leached species (see Section 2.2), but he did not discuss how these leach tests related to the static conditions in which the samples were weathered. In subsequent work, the cutoff point between weathered and unweathered glass was set at 60 mol.% "SiO_2" [COX-1979], based on a composition-appearance correlation.

Medieval glasses have also been exposed to dynamic weathering conditions. Fewer samples of this type of weathering have been reported, probably because, as noted by Newton, corrosion under static conditions is far more extensive than under dynamic conditions. This comment, however, may be based more on appearance than on detailed measurement because in examining reacted regions of windows presumably exposed to dynamic conditions, Cox [COX-1979] found pits with depths of several millimeters, comparable to the layer thickness found on crusted glass. Additionally, in the controlled weathering tests of Fuchs et al. [FUCHS-1991], no difference was noted in the extent of reaction between static and dynamic exposures; the change in infrared absorption due to crust formation (static weathering) was equivalent to that for leached layer formation (dynamic weathering). In the cases of extremely wet exposure (contact by rain water), the dynamic corrosion exceeded that due to static weathering.

Comparison of the results of commercial (see Section 3.1) and conservation-based studies shows qualitative similarities. Under static weathering, alkalis leached from the glass are concentrated on the glass surface and undergo further reaction with either gases from the air, groundwater components, or other elements released during network hydrolysis. However, in the studies on commercial or historical glasses, no quantitative description is given of the secondary phases formed within the crust or reacted layer and their role in the reaction process is not clear. If runoff occurs as in dynamic weathering, the reaction products are carried away, the buildup of alkali in the contacting solution is diminished, and subsequent dissolution of the glass matrix may be delayed. However, the silica-rich layer formed during the alkali-depletion process may crack and exfoliate, exposing fresh surfaces for the reaction sequence to continue.

3.3 Natural Glasses

Under static weathering conditions, the same type of corrosion processes are observed for natural glasses as described for commercial glasses. These processes are observed in nature and can be reproduced in the laboratory. Initially, obsidian undergoes a water-diffusion process without accompanying dealkalization and remains stable for thousands of years [MAZER-1992a]. Tektites and obsidian undergo the initial alteration due to water diffusion, but after hundreds of thousands to millions of years, restructure into clay phases that have remained intact under burial conditions. This restructuring may include a dealkalization process depending on the composition of the clay phases and the original alkali content of the glasses. Basaltic glasses, which have a lower silica content, undergo a dealkalization process and transform into a range of minerals in a process similar to HLW glass (see Section 5).

3.4 Static Weathering of HLW Glass

The reaction of HLW glass with water vapor has been examined in a series of studies done at Argonne National Laboratory (ANL). Other studies have exposed HLW glass to vapor [PICKERING-1980; YOKAYAMA-1985] in short-duration tests, and 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) the WVCM 44, WVCM 50, ATM-10, and PNL 76-68 compositions designed for the reprocessing of commercial fuel; 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. A relative humidity chamber was used for tests done below 100% relative humidity, whereas a sealed system was used for tests done at 100%. The initial amount of water in the system was controlled because it was observed that dynamic weathering (refluxing) could occur if liquid was present [EBERT-1991a]. Results were considered valid only if the relative humidity remained at 100% throughout the test period and no refluxing occurred. During static weathering, it was observed that the glass generally altered to form a reacted layer that penetrated into the glass and secondary phases on the surface of the glass [EBERT-1991b; BIWER-1990]. The alteration of HLW glass generally results from redistribution of elements that make up the original glass structure. The alteration layer generally contains Fe- or Mg-rich clays with varying degrees of crystallinity. Segregation of actinide elements within the layer to form stable calcium phosphate or Ti phases has also been observed [BATES-1992a, -1992c]. Because sufficient liquid is not available for analysis, the extent of reaction is monitored through the development of secondary phases, the thickness of the reacted layer, and weight gain. A typical reacted layer and glass surface showing these features is shown in Fig. 3-1d. For comparison, this figure also includes samples of commercial, historical, and natural glasses that have been exposed to static weathering.

The factors that affect static weathering have been reported to be time, temperature, glass composition, volume of water contacting the glass, vapor composition, and radiation. An overview of the experimental results as a function of each variable is presented in Sections 3.4.1 through 3.4.6. Interpretation of the experimental results is presented in Section 3.5.

3.4.1 Time

Except for R7T7 glass, two distinct reaction stages have been noted in the weathering process. An initial stage is parabolic with time and is the stage during which an alkali-depleted layer forms. A second more rapid stage is marked by secondary phase formation [BATES-1982a; ABRAJANO-1989; EBERT-1991a, -1993c].

During the initial reaction stage, limited secondary phase formation occurs on the surface and distinct differences are observed for the various glasses. PNL 76-68 and R7T7 glasses undergo very little reaction, except under high-temperature conditions, and show limited surface alteration or Na depletion. However, the weight-change measurements for PNL 76-68 glass do show a parabolic gain as a function of time [ABRAJANO-1989]. The other glasses form a distinct altered layer. The observation of two types of layer formation suggests that two processes may occur during the initial reaction stage, both showing a parabolic dependence with time. In one case, the glass hydrates without dealkalization, no phases form on the surface, and no clay layer is observed. In the other case, dealkalization of the layer occurs, Na-bearing phases may form on the surface, and the layer restructures to a clay. This latter example is also typical of the static weathering of commercial and natural glasses.

The second reaction stage is characterized by a rapid increase in the reacted layer thickness (Fig. 3-2d) and the formation of precipitates. The time necessary for the onset of this stage is difficult to reproduce. Except for R7T7 glass, this reaction process dominates the long-term reaction. The onset and continuation of the increased corrosion rate have been related to phase precipitation [BATES-1982a, -1982b; EBERT-1991a]. When precipitation occurs, the affinity for glass reaction may increase and result in an increased reaction rate. The temporal variations in the onset of secondary phase nucleation leads to variations in layer thickness; however, the general rate trend for the second reaction stage is linear, which is consistent with an affinity-controlled reaction [EBERT-1991a].

3.4.2 Temperature

The static weathering of historical and commercial glasses under ambient conditions is a relatively slow process. In studies of HLW glasses, temperature is often used as a means of accelerating the corrosion process to project glass dissolution to long time periods (see Section 2.4).

To use temperature as an accelerating factor, the reaction mechanism must not change over the temperature range of interest. Mazer et al. [MAZER-1991b] have described such a case for obsidian, where one process--molecular water diffusion--is the dominant process. Reaction rates were determined over a range of temperatures and the rate constants were fit to the Arrhenius equation to obtain the activation energy for the reaction. With HLW glass, for which several mechanistic processes may determine the rate, the use of temperature as an accelerating factor may not be as straightforward because the rate-determining process may change with time and reaction progress. The approach taken by Abrajano et al. [ABRAJANO-1989] to examine the validity of using temperature for acceleration was to determine the rate constant of the initial parabolic stage of the reaction progress as a function of temperature, compare reaction products, and examine the detailed structure of the reacted layer. The most complete data set is for SRL 131 glass which has been tested between 75 and 240°C. Tests were conducted over a 10-year period by different researchers and under different conditions (Fig. 3-2d) [BATES-1982a; ABRAJANO-1989]. Figure 3-3 shows the similarity in reaction products observed at 75 and 200°C plus the Arrhenius fit of the rate constant for the initial

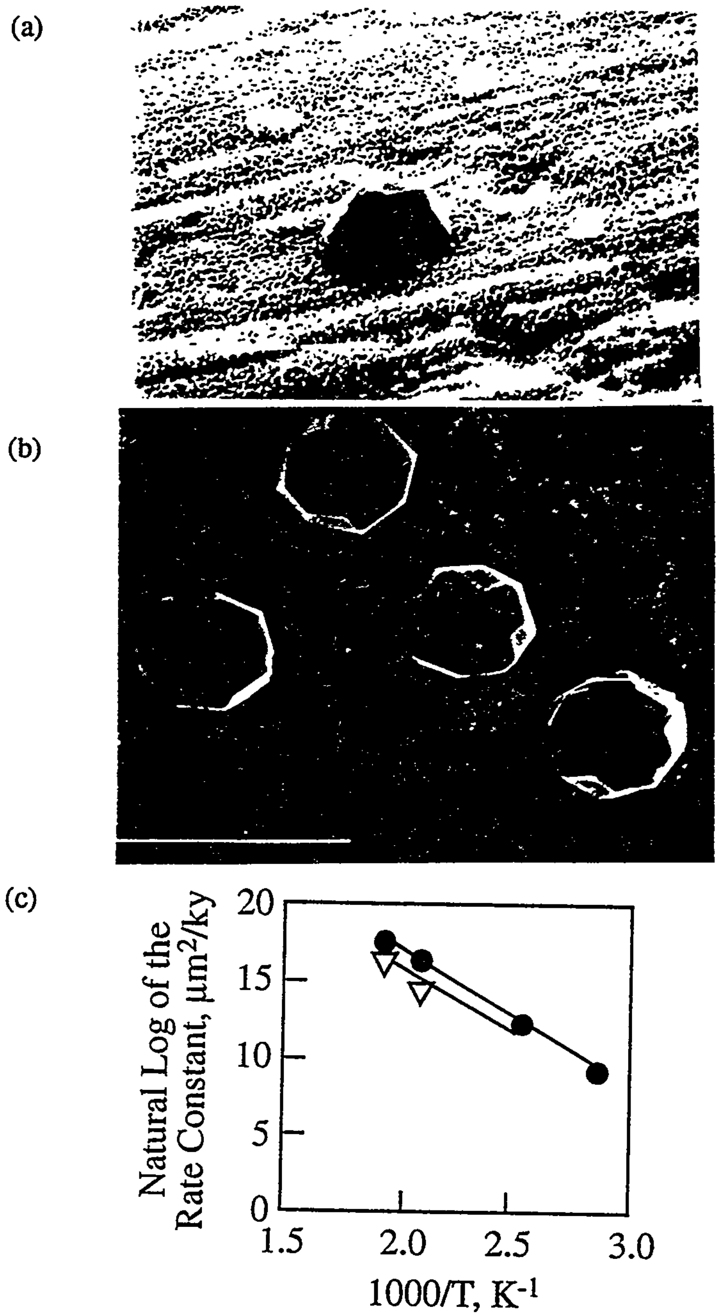

Fig. 3-3. Comparison of Secondary Alteration Products that Form on the Surface of HLW Glass when Exposed to Static Weathering Conditions at (a) 200°C and (b) 75°C (adapted from [BIWER-1990]). An Arrhenius relationship for the alteration rate for the initial stage of static weathering is shown in (c). The similarity in alteration products observed at the two temperatures based on trapozedral morphology, composition, and X-ray diffraction data, plus the good fit to the Arrhenius plot, suggest that the reaction mechanism for the initial stage of static weathering is the same over the temperature range 75 to 200°C and that tests done at elevated temperatures can be used to accelerate processes occurring at lower temperatures where (•) represents SRL 131 data and (∇) represents SRL 211 data (adapted from [ABRAJANO-1989]). Analcime is the product with the trapozedral morphology and the glass surface is a smectite clay.

stage of the reaction over the entire temperature range. An Arrhenius-type rate law fits the data well [ABRAJANO-1989] and, when combined with identification of the same phases forming on the glass surface over the entire temperature range [BIWER-1990] plus a similarity in the structure of the reacted layers, suggests that the same reaction mechanism controls the glass corrosion during the initial kinetic stage over the temperature range studied.

3.4.3 Glass Composition

Compositional effects on the weathering processes have been observed for the range of glasses studied. The static weathering of HLW glass can occur in two stages: (1) an initial dealkalization stage dominated by water diffusion and (2) a second stage characterized by the formation of secondary phases and a rapid increase in reaction layer thickness (see Section 3.4.1). For the second stage to occur, the solution chemistry of the thin film of water on the glass (e.g., pH and elemental concentrations) must be able to support secondary phase formation, and nucleation of the phase must occur. Once the phase forms, the concentration of elements in solution changes, the reaction affinity increases (see Volume I, Section 3.3.2), and the rate of reaction increases. One of the first phases to form during weathering of HLW glass is the zeolite analcime ($NaSiAlO_6 \cdot H_2O$). A good example of composition affecting the dominant reaction process has been reported for PNL 76-68 glass [ABRAJANO-1989]. When PNL 76-68 glass was exposed to static weathering conditions at 200°C, the first process to occur was dealkalization and the Na concentration on the surface increased. However, because this glass does not contain a significant amount of Al, analcime could not form and consume the Na. The Na concentration on the surface increased to the point where alkali release was quenched and the dealkalization reaction stopped. Thus, the second stage of reaction was never attained during the test periods. The onset of stage two depends on the glass composition, and the glass composition may be able to be tailored to avoid crystal formation.

The effect of analcime formation on glass reaction under saturated conditions has also been studied by Van Iseghem and Grambow [VAN ISEGHEM-1988a] through testing and modeling. Here it was shown that the silica-to-alumina ratio in the glass was a factor controlling whether analcime formation would occur, thus resulting in a transitory silica saturation stage and a "final" reaction rate greater than that without analcime formation.

For other HLW glasses, the dealkalization process proceeds to the point where secondary phases form and rate constants for the initial dealkalization stage of the reaction can be derived at each temperature. An Arrhenius plot can be used to evaluate the reaction process. The data for SRL 211 and 131 glasses are plotted in Fig. 3-3. The slopes of the curves are similar, indicating that the activation energies (about 80 kJ/mol) for the processes are similar. The similar activation energies, plus the observation of the same secondary phase forming on each glass, suggest that the reaction process is the same for each glass.

A systematic comparison of compositional effects was done using SRL 131 as the base composition [DIEBOLD-1986; CROMWELL-1990]. The amount of Na and Li in the glass was varied, keeping the total alkali amount constant. The results of static weathering experiments done at 200°C were consistent with dealkalization being the dominant reaction process during the initial stage of reaction. As the Na content of the glass increased, the reaction rate increased; however, the effect of Li was not as significant.

3.4.4 Volume of Water (Vapor Contact)

During vapor hydration, reaction usually takes place between a thin film of sorbed water and the glass surface [EBERT-1991c]. The thickness of this film varies as a function of relative humidity and time as components from the glass become dissolved in the film [EBERT-1991c]. The initial glass/vapor interaction has been studied for a variety of glass types, ranging from glasses high in silica content to natural glasses [HAGYMASSY-1969; BRUNAUER-1938; CMT-1992] and HLW glasses [EBERT-1991c]. When glass is exposed to water vapor, water sorbs onto the glass surface by chemical and physical forces. The amount of water contacting the surface in equilibrium (without reaction) with the vapor is measured in carefully controlled experiments, and the results are presented by a sorption isotherm in terms of number of monolayers vs. relative humidity (Fig. 3-4). The data for several glass types show that little or no sorption (<1 monolayer) occurs at relative humidities below 50% and that a general coverage of 1 monolayer occurs at 50% relative humidity. Infrared spectroscopy studies suggest that water is initially sorbed onto silanol groups and then forms clusters as the humidity increases [PASHLEY-1979]. As the relative humidity exceeds 90%, the number of monolayers increases rapidly.

Comparison of the sorption behavior of simple glasses to more complex HLW glasses provides insight into the initial interaction between the glass and water vapor. Isotherms for two different glass types are shown in Fig. 3-4 to highlight how differences in glass composition affect the amount of water sorbed. Obsidian is a naturally occurring silicate glass with a low alkali content, while SRL 165 is a reference HLW glass composition containing about 20 wt.% alkali oxides. The shape of both curves is similar, but obsidian sorbs only 5 monolayers at saturation, while SRL 165 glass sorbs about 40 monolayers [EBERT-1991c]. This suggests that, while the mechanism for water sorption is similar on the two glasses, the alkali content of the glass influences the amount of water that is sorbed. Alkali in the glass may affect the sorption in two ways: alkali on the surface may provide additional sorption sites, and alkali released from the glass into the sorbed film via ion-exchange reactions effectively lowers the vapor pressure of the film causing additional water vapor to condense in the film to maintain equilibrium between the film and the vapor. Thus, glasses with relatively high alkali contents, including HLW glasses, have a greater sorption capacity than glasses with small alkali contents, such as obsidian. The amount of accumulation will also depend on the exposure time. At relative humidities below about 70%, the amount of alkali released is small due to the limited amount of water available for reaction, so neither sorption nor ion exchange proceed to a significant extent [ABRAJANO-1989]. At higher relative humidities, enough water is sorbed to initiate the release of alkalis, which in turn increases the amount sorbed.

3.4.5 Vapor Composition

As discussed for simple alkali-silicate glasses (Section 3.1) and historical glasses (Section 3.2), reactive gases in the vapor can affect the chemistry at the glass-vapor interface,thereby influencing the physical nature of the altered surface and the actual reaction products formed [CHAO-1982; CHEN-1981]. As discussed earlier, sulfate or carbonate precipitates may form as a result of reaction with SO_2 or CO_2. Sulfate species have been described as either protective (short-term) due to the formation of a silica-rich surface layer [CLARK-1979] or deleterious because of their capacity to promote ion-exchange reactions by acting to scavenge alkali when present in the vapor at a high level [RAY-1976; PEREZ-y-JORBA-1990]. Additionally, radical species generated in controlled laboratory tests have been suggested to increase the hydration rate for both simple and HLW glasses

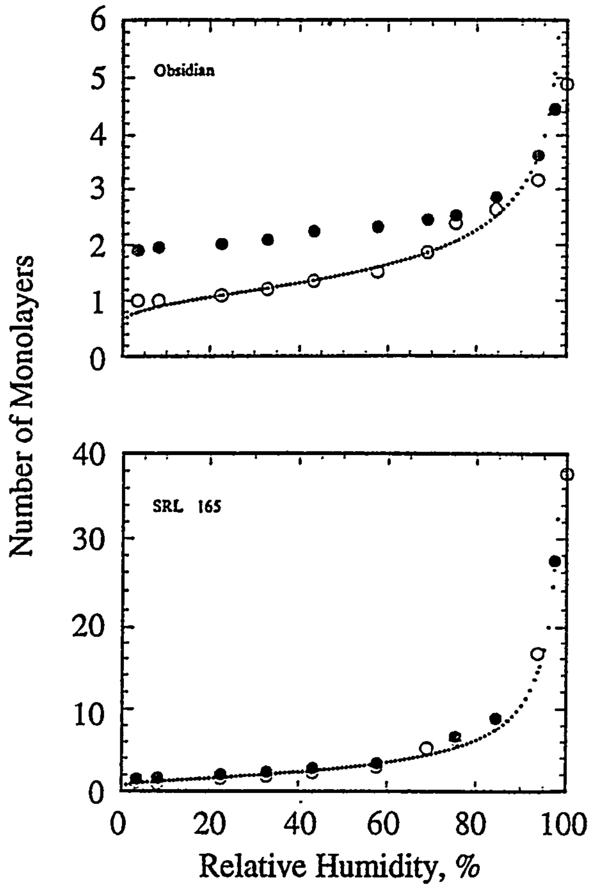

Fig. 3-4.
Sorption Isotherms for Water on Obsidian, an Alkali-Poor Glass, and a HLW Glass with a Greater Alkali Content. The number of monolayers of water sorbed to the glass increases as the alkali content increases (adapted from [EBERT-1991c]), (o) adsorption, (•) desorption.

[WRONKIEWICZ-1991] (Section 2.5.3). Also, Fuchs et al. [FUCHS-1991] have noted that low-stability glass sensors react most rapidly when exposed to an atmosphere enriched in oxidizing agents like NO_2 and O_3, suggesting that these species may also play a role in accelerated glass alteration as observed in radiation tests.

In an experiment conducted with Boom clay in Belgium, glass was exposed to a clay vapor environment where vapor, after being forced through the clay, entrained substantial quantities of chloride, sulfate, and phosphate. Experiments were done over a range of temperatures up to 170°C; although the control over conditions was poor (the samples in some cases were contacted by liquid water also), some insight can be gained by examining the results [VAN ISEGHEM-1989, -1990a; ODOJ-1981]. Glass reacted in the vapor demonstrated little change in sample mass, which was taken to mean that no significant release of radionuclides would occur under these conditions. However, when the vapor-reacted glass was also contacted by liquid water, considerably more reaction was observed compared with static leaching. After 16 months of alternating vapor-liquid contact at 90°C, it was determined that some of the glass samples had completely reacted through their 3 mm thickness. This compares to a reaction of less than 100 µm that occurred due to static leaching at 90°C [VAN ISEGHEM-1989].

Carbonate and sulfate species have also been observed on the surface of SRL 131 and SRL 165 glasses exposed to air at 75°C and relative humidities of less than 100% [BIWER-1990]. The air contained only trace amounts of SO_2 and CO_2 but, because the relative humidity was below 100%, the first-stage dealkalization process was slowed and interaction was observed between the released alkalis and the acidic components of the vapor. When the experiments were repeated at 100% relative humidity, the amount of sulfate and carbonate phases was overwhelmed by secondary products resulting from hydrolysis of the glass network. Although limited, the available results examining the effect of reactive components carried by vapor on the static weathering of HLW glass show that, when present in sufficient quantity, these components can affect the course of the glass reaction.

3.4.6 Radiation

Radiation exposure of glasses under the relatively high S/V conditions that exist when glass is exposed to water vapor leads to rapid concentration of radiolytic products in the relatively limited amounts of water condensed on the glass surface [McELFRESH-1983; WRONKIEWICZ-1993].

Wronkiewicz et al. [WRONKIEWICZ-1993] performed tests under saturated air-vapor conditions to examine the effect of both gamma and alpha radiation at bounding levels that would exist during storage. Alpha radiation effects were studied by exposing a water-saturated vapor environment to a alpha field of about 5 x 10^3 rad/h generated by an inert metal foil doped with ^{241}Am. These studies demonstrate that an alpha field in a moist air environment was effective in interacting with the air environment in the reaction vessel to produce radiolytic products that become concentrated in the small volume of liquid present. Similar studies with gamma radiation were done with no glass present to extend the work of Burns et al. [BURNS-1982a] to gamma dose rates in the 10^4-10^5 rad/h range. Thus, it has been demonstrated that radiolytic products produced due to both alpha and gamma radiolysis become concentrated in small volumes of liquid under high S/V conditions.

The resultant effect of these radiolytic products on glass weathering have also been examined by Wronkiewicz et al. [WRONKIEWICZ-1991, -1993]. Tests were done using a glass doped with Am, Pu, and Np, and this glass was exposed to a vapor environment in an external gamma field of about 5 x 10^3 rad/h. This combination of alpha/gamma fields is similar to that expected during the early stages of storage and represents a bounding case for radiation exposure. In these tests the atmospheric bicarbonate present in the small volume of condensate may be neutralized by nitric acid produced in radiolytic reactions, and any nitric acid that subsequently accumulates on the glass surface is likely to react with the glass, significantly accelerating the glass dissolution process. In these combined gamma and alpha radiolytic tests under high S/V conditions, alteration layer development was observed to occur 10 to 15 times faster than corresponding tests run without radiation [WRONKIEWICZ-1993]. Both the diversity and total quantity of secondary alteration products on the glass surface increased in tests run with external gamma exposure [YOKAYAMA-1985; WRONKIEWICZ-1991, -1993]. Similar effects of acid gases in accelerating glass reaction have also been observed in controlled atmosphere studies of historical window glass [FUCHS-1991].

3.5 Interpretation of Experimental Observations on Static Weathering

From the information available on the static weathering of commercial, historical, simple alkali silicate, natural, and HLW glasses, a consistent set of observations can be made. Such 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 with the corrosion rate decreasing with time. However, after very long periods of time or under accelerated test conditions, the corrosion rate can increase, resulting in the generation of thick reacted layers. These layers are alkali-depleted, and they exhibit composition segregation and some degree of crystallinity. Continued reaction appears to be linear with time. The extent of crystallization increases with time, and secondary phases form on the glass surface as a result of either recombination with atmospheric gases or of restructuring of elements leached from the glass. The onset of the second-stage reaction has been described as due to a decrease in the solution concentration of elements that control the reaction affinity of the glass [EBERT-1991a].

Abrajano et al. [ABRAJANO-1989] have described the first-stage reaction process in terms of the reactions shown in Table 1-1 and the associated transport and reaction steps that control the rate. The reactions in Table 1-1 have been discussed previously in terms of glass corrosion, but each reaction may also occur during static weathering. Hydrolysis can occur at the boundary between the glass and the reacted layer and in the gel layer, and may be a gradual process where large silica-based fragments are formed and gradually broken down. At the outer surface of the layer, network dissolution (reaction 4 in Table 1-1) may occur--which may result in dissolution of the Si units in the thin film of water and lead to the formation of secondary phases on the surface. Network hydrolysis is a process with a high activation energy [ABRAJANO-1989]. However, hydrolysis might be necessary before dealkalization can occur. The hydrolysis of NBO sites in the glass may promote the reaction of molecular water with bridging oxygen bonds. Abrajano et al. favor a transport-controlled process, either ionic interdiffusion or molecular water diffusion, as the rate-controlling step for the first stage reaction.

3.6 Dynamic Weathering of HLW Glass

In a series of tests developed specifically to study the reaction of HLW glass when exposed to dynamic weathering, Bates et al. contacted glass with regulated amounts of dripping water at 90°C [BATES-1985, -1986b, -1990c; WOODLAND-1991]. These tests have extended for long periods (six years) and have monitored the reacted glass surface and the release of glass components and actinide elements to solution. The dynamic weathering tests were designed to study glass reaction when exposed to a variety of glass/water contact modes, including contact with moist air followed by periodic rinsing of the surface, contact between glass and standing water, and interactive effects with metal components of an engineered barrier system. The tests were performed so that the solution composition could be continuously monitored and the reacted glass examined periodically.

Because of the variability in conditions that might occur in an unsaturated environment, the dynamic weathering tests of HLW glass were done to study the effects of a range of parameters, including water contact interval, surface area of the glass, water volume, glass composition, and stainless steel sensitization. The results of these tests are illustrated in Figs. 3-5 and 3-6 with the results of aqueous corrosion tests on similar glasses. The results for boron are illustrated in Fig. 3-5 and are representative of the glass matrix reaction; Pu results shown in Fig. 3-6.

The surface layer for SRL 165-type glass forms in a way that is only weakly attached to the base glass [WOODLAND-1991]; during periodic flow, some of this layer was dislodged from the surface. Because any material that is released from the glass surface (either dissolved in solution, suspended in solution, settled from solution, or sorbed onto metal components) was included as part of the normalized elemental release, the release trends reflect spallation. Evidence for spallation has been observed for several test configurations [WOODLAND-1991], both in the solution results and in examination of the reacted glass. After about two years of testing, an increase in Si release was

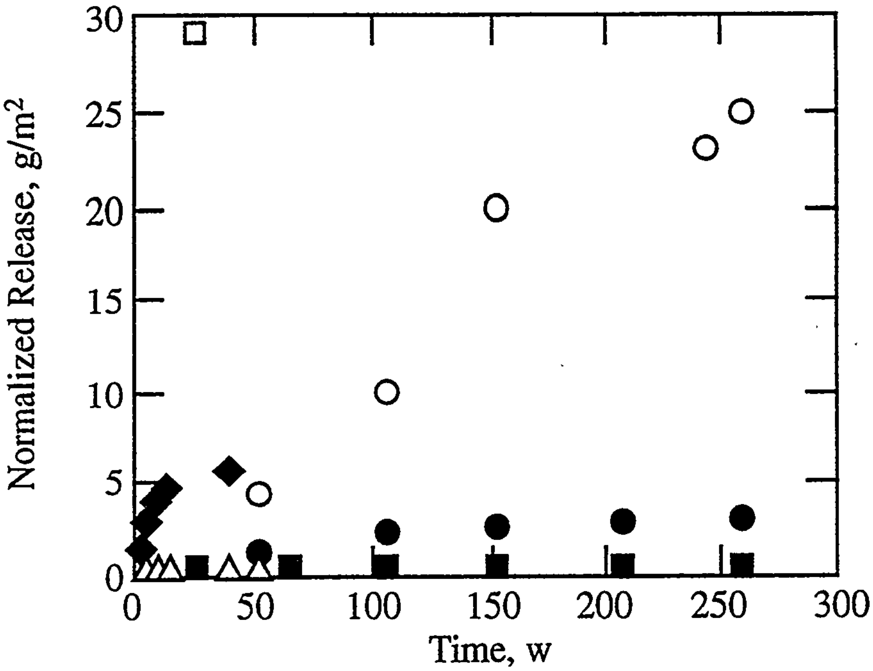

Fig. 3-5. Normalized Release of B from SRL 165 HLW Glass Reacted under Various Conditions (○) Drip Tests with Major Spallation (adapted from [WOODLAND-1991]); (♦) MCC-1 Type Tests with EJ-13 Water at S/V = 30 m^{-1} (the uncertainty of the data falls within the size of the data points) (adapted from [EBERT-1990b]); (•) Drip Test with Moderate Spallation (adapted from [WOODLAND-1991]); (△) Periodic Exchange Test at S/V of 2000 m^{-1} and Exchange of 6% per Period, Deionized Water; (■) Periodic Exchange Test at S/V of 2000 m^{-1} with J-13 Water and Exchange of 25% per Period, Complete Exchange in One Year; (□) SRL 165A Glass, Leaching of Vapor Hydrated Glass at S/V about 30 m^{-1}, EJ-13, and Total Aliquot (adapted from [BATES-1990a]). All tests were done at 90°C. The greatest B release is observed in the tests done at low S/V and when the layer spalls from the glass. Less release is observed when there is an accumulation of reaction products in solution as occurs in the periodic exchange tests.

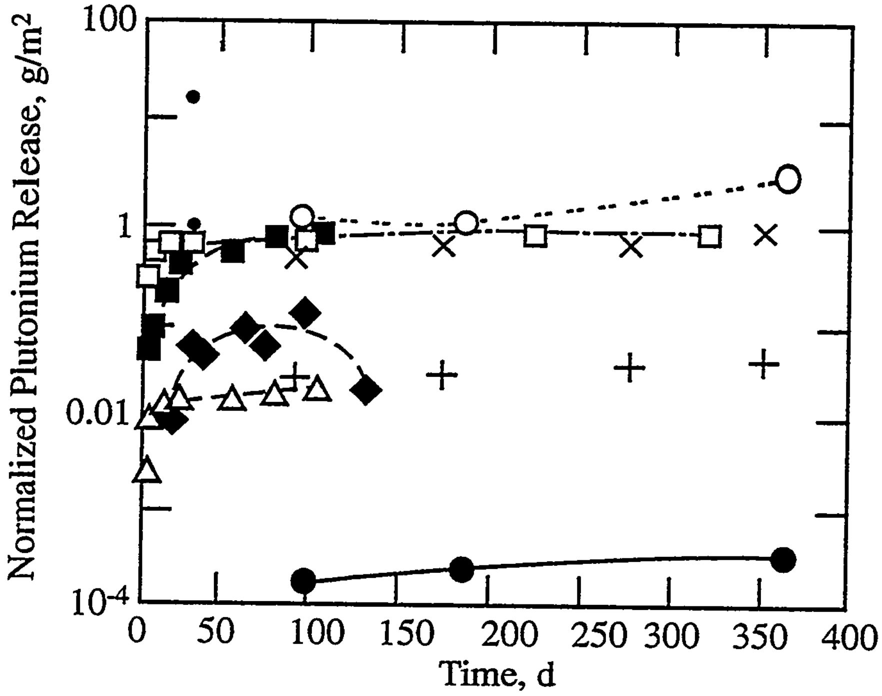

Fig. 3-6. Normalized Release of Pu from Various Glasses under Various Conditions: (○) JSS/A glass, S/V = 1100 m^{-1}, 90°C, 0.45 μfilter, no acid strip, deionized water (adapted from [WERME-1990]); (♦) SRL 165/42 glass, S/V = 100 m^{-1}, 90°C, J-13 water, no filtering, no acid strip (adapted from [BIBLER-1987]); (■,•) SRL 165A glass, leaching of vapor hydrated glass at S/V about 30 m^{-1}, 90°, EJ-13, unfiltered and total (unfiltered plus acid strip) (adapted from [BATES-1990a]); (□) SRL 131/11 glass, leachate replaced periodically, 40°, deionized water, S/V = 10 m^{-1}, fractured glass, unfiltered with no acid strip (adapted from [BIBLER-1982b]); and (■) SRL 165A glass, S/V = 30 m^{-1}, EJ-13 water, acid strip included (adapted from [EBERT-1990b]), (x) SRL 165A glass, dynamic weathering conditions, EJ-13 water, acid strip included (adapted from [BATES-1990c]), (*) SRL 165A glass, dynamic weathering conditions, EJ-13 water, no acid strip, no filtering (adapted from [BATES-1990c]).

correlated with gaps in the layer on the reacted glass, which was also correlated with a greater amount of spalled products in the test solution. In these tests, the boron release increased continuously with time rather than exhibiting saturation control (compare drip test results with leach results in Fig. 3-5).

The results obtained in dynamic weathering tests have shown a range of releases and release patterns. Bates et al. [BATES-1990a] have conducted tests where pre-hydrated glass was exposed to a static MCC-1 test for 28 days. At the end of the test, Pu and Am in the unfiltered leachate and in an acid strip of the test vessel (together with the glass support stand) were determined. Although the Pu and Am results for the leachate and acid strip were reported separately, the total amount of Pu and Am found in the leachate together with that found in the acid strip was referred to as "released". Thus, for the discussion of these tests, the word "released" embraces the fraction of the actinides that is found at the end of the test to be no longer physically attached to the glass substrate (i.e., it includes dissolved, sorbed, colloidal, suspended particulate and exfoliated material). It is important to recognize that this use of the word "release" differs from the glossary definition.

For tests where pre-hydrated glass was subsequently exposed to a static MCC-1 type test for 28 days, the total Pu release is about 50% of the B release (compare data in Figs. 3-5 and 3-6, particularly the normalized Pu release data for pre-hydrated glass). However, the majority of the Pu was associated with spalled layers that were not suspended in solution [BATES-1990a]. In fact, when only the Pu fraction found in the unfiltered leachate is considered to be "released" (consistent with the glossary definition), then the Pu release fraction for these tests is in the 2-4% range [BATES-1990a] which is consistent with the results reported elsewhere for aqueous corrosion conditions (see Section 2.7.2).

Actinide release is controlled by several factors. If an actinide element is retained in the spalled material, its release is subject to the factors that affect spallation. If the actinides dissolve in solution, their release may be limited--depending on their solubility and distribution between metal and solution. Plutonium and Am have very low solubilities (10^{-10} to 10^{-12} $\underline{M}$) in basic pH systems [EBERT-1990b] and also sorb strongly to metal components in the test material [BATES-1990a; EBERT-1990b; VERNAZ-1991a]. Based solely on the leachate fraction, for actinide-doped 165-type glass, normalized Pu, Am, and U release were generally ten to hundred times less than the glass reaction whereas Np release ranged between 30 and 100% of the boron release [BATES-1990c]. However, if the actinide fraction associated with the test vessel and associated metal components together with the fraction suspended in the leachate are taken into account, the total normalized release of all actinides, $(NL)_{act}$, approaches that of the glass. Through 52 weeks of testing, B and actinide releases (g/m^2) [BATES-1990c, Table 10] are reported as: 13 weeks - $(NL)_B = 0.35$, $(NL)_{Pu} = 0.3$, $(NL)_{Am} = 0.4$; 26 weeks - $(NL)_B = 1.3$, $(NL)_{Pu} = 0.7$, $(NL)_{Am} = 1.1$; 39 weeks - $(NL)_B = 1.1$, $(NL)_{Pu} = 0.5$, $(NL)_{Am} = 0.7$; 52 weeks - $(NL)_B = 0.8$, $(NL)_{Pu} = 0.6$, and $(NL)_{Am} = 0.7$. Patterns of actinide release from these dynamic weathering tests are also shown in Fig. 3-6 for comparison with aqueous corrosion tests done with fully radioactive glasses.

With ATM-10 glass, the Pu and Am distributed to a Ca-Th-PO_4 phase, brockite, which was contained within colloidal clay particles suspended in solution [BATES-1992a]. During dynamic weathering, nearly 100% of the Pu and Am detected in the leachate was associated with this suspended material. In these tests, the Pu and Am phases formed within the reacted layer prior to release into solution, which in general is different from tests done under saturated conditions. Under saturated conditions, if congruent dissolution of the glass occurs, the Pu and Am are attracted to colloids that form in solution or to metal components of the test and thus do not remain in solution. In the tests discussed here [BATES-1992a], the amounts of Pu and Am associated with the metal components have not been reported, so a full accounting of the distribution of Pu and Am between solution (potentially transportable) and sorbed to metal components (presumably non-transportable) cannot be determined. Also, no evidence was presented related to the transport properties of these colloids. With SRL 131 and SRL 202 glasses, a U-Ti phase formed within the clay layer [ABRAJANO-1990b; BATES-1992c]. In these dynamic weathering experiments, actinides remained in the leachate because they were associated with colloidal material; their speciation can be contrasted to that of R7T7 glass (under either static or saturated flow conditions) where the release of Pu is thought to be controlled by plutonium oxides and hydroxides retained within the layer and spallation has not been observed [VERNAZ-1991a]. The Pu and Am distribution in solution and the fraction available for transport is dependent on the glass composition, the water contact scenario, and the redox environment. Neptunium and U have higher solubilities, and their normalized release values generally approach those of B and Li, regardless of glass/water contact conditions [VERNAZ-1991a; EBERT-1990b].

To relate laboratory tests to processes that may occur during disposal, several examples are particularly relevant to an unsaturated environment. At an unsaturated burial site in Ballidon, U.K., a variety of glasses ranging from commercial to historical to HLW have been set at approximately ground level and covered with crushed limestone [NEWTON-1985c (and references therein); WICKS-1988; NAMBOODRI-1991]. An alkaline pH environment was created to monitor glass weathering, and the site is kept at ambient temperature and subjected to frequent water contact. Glass samples have been retrieved at set intervals for up to four years, and the commercial and historical glasses have been examined visually. In most cases, very little alteration has occurred. The HLW glasses, examined using SIMS, show layer formation that consists of an outer layer derived from glass leaching and interaction with groundwater; this layer has sequestered Cs and Sr. The glass itself was reacted to a depth of 0.2 and <1.0 μm after one and two years, respectively. In laboratory tests static weathering at 75°C and 95% relative humidity yielded yearly rates of about 0.5 μm/yr for SRL 165 glass and 6 μm/yr for SRL 131 glass [BIWER-1990; BATES-1992b].

3.7 Radionuclide Release

The potential exists that HLW glass could be exposed to conditions supporting either static or dynamic weathering. Although the potential for these types of alteration is greatest under unsaturated conditions, glass in a saturated repository environment might also be exposed to water vapor (static weathering) as water entered the void space in the pour canister and vaporized [BATES-1984b]. Static weathering causes an alteration or aging of the glass that may affect radionuclide release patterns [SEITZ-1984a]. The only method for release of radioactivity from the glass is through contact with liquid water. During static weathering, liquid water contact is initially limited to the thin film of water that sorbs to the glass surface in a humid air environment. However, as the film becomes concentrated in elements leached from the glass, the vapor pressure of the liquid is lowered and more water condenses on the surface (i.e., water may accumulate on the reacting glass in a humid air environment) [CUNNANE-1991b]. This process has been examined during the weathering of HLW glass where the concentration of elements in the condensed film was measured [EBERT-1991b] and the refluxing of the glass during the hydration process was suggested [CUNNANE-1991b]. The application of such a scenario to both high- and low-level waste burial sites has been recognized as a means by which, in a strictly humid atmosphere, condensed water could be a pathway for radionuclide release [CARY-1991].

Glass that has aged via static weathering could be contacted later by liquid water. The leaching response of the weathered glass has been addressed in flowthrough, static, and drip tests of glass doped with transuranics and radiotracers and of fully radioactive glass. Seitz [SEITZ-1984b] exposed weathered PNL 76-68 glass to a flowing system representative of a simulated basalt repository (90°C, 0.5 mL/h) and reported increases after 110 days in radionuclide releases of Pu (70-fold), U (200-fold), and Cs (50-fold) compared with an unweathered glass. He also noted that the release of some elements actually decreased due to weathering. There was a twofold decrease in Ba in solution, which suggests that Ba was incorporated into a phase that formed during the weathering process.

Bates [BATES-1984a, -1990a] has conducted static tests with transuranic-doped SRL 131, SRL 165, and ATM-10 glasses. The objectives of these tests were to compare leaching from hydrated and nonhydrated glass and to identify issues to be resolved in the long-term testing of glass. The comparative tests were MCC-1 type conducted for short time periods at 90°C. Differences in the release of major glass components (Li, Na, B, Si) were observed as a result of the secondary phases that formed during weathering. Each of these elements increased in solution in the tests with weathered glass. Additionally, the release of Pu and Am to solution as a transportable fraction (dissolved and suspended) increased up to 1000-fold for weathered glass [BATES-1990a]. The amount of increase was a function of the degree of weathering. However, the actual dissolved fraction had low concentrations of Pu and Am (Pu = 5×10^{-10} and Am = 4×10^{-12} M), which are comparable or lower than the values reported for leaching of nonweathered glass [EBERT-1990b]. During weathering, the transuranic elements may be isolated in secondary minerals [BATES-1989, -1992a]. The conclusion is that, if weathered glass were contacted by groundwater, actinides might be released as a colloidal fraction rather than a dissolved fraction.

Dynamic weathering tests have been performed on fully radioactive as-cast and weathered SRL 200R glass [BATES-1993]. A silicate groundwater was dripped on the glass surface at 90°C and the leachate was analyzed after it had dripped from the glass. The cations and anions present in the leachate are listed in Table 3-2, which shows that a concentrated salt solution is formed for the weathered glass. Significantly, the concentrations of sulfate and phosphate are higher than those observed for as-cast glass, and the pH has increased from about 8.5 to 11.8. However, the actinide fraction (Pu and Am) in the weathered test solution is almost totally dissolved in solution, rather than being in suspension, as was observed in the dynamic weathering tests of ATM-10 glass (see previous discussion). The dissolved concentrations are also greater than those found in the batch leach tests of hydrated glass (Fig. 3-6) by several orders of magnitude, probably because of the complexing nature of the anions [KIM-1991a]. (See Section 2.7 for discussion of actinide complexation.)

From the above observations and as shown in Fig. 3-6, if hydrated glass is contacted by liquid water, the initial release of activity is higher compared with fresh glass. The amount of material released to solution depends on the extent of weathering and, depending on the mode of water contact (immediate submersion or dynamic weathering), may result in radionuclides suspended in solution as colloids, and as complexes dissolved in solution, or partitioned to mineral phases. For comparison, the actinide releases from a range of tests are shown in Fig. 3-6.

Table 3-2. Comparison of Solution Composition after Four Months from Drip Tests Done with Fully Radioactive SRL 200R Glass. Test conditions were 90°C with a water contact rate of 0.075 mL every 3.5 days [BATES-1993]

	Concentration (ppm)	
	As-Cast	Aged
Li	10	1000
B	10	20,000
Na	100	40,000
Si	50	1500
Cl^-	9	200
$SO_4^=$	100	8000
$PO_4^=$	0	400

3.8 Summary

- Glass weathering is alteration that occurs between glass and humid air or intermittent water contact. The alteration modes can be further identified as static weathering, where water sorbs onto the surface in thin films and reacts with the glass, or dynamic weathering where water vapor contacts, condenses, or sorbs to the glass surface, accumulates, and eventually runs off the surface. Both weathering processes simulate the corrosion conditions to which glass may be exposed in an unsaturated environment.

- The alteration of glass as studied by the commercial glass industry provides insight as to important physical parameters and reaction mechanisms that are important under weathering conditions. These parameters include relative humidity, glass composition, time, and temperature. The reaction mechanisms are similar to those identified for aqueous corrosion of glass. In weathering, the formation of secondary phases occurs readily due to the high S/V conditions and has a pronounced effect on further reaction.

- The importance of the physical parameters in weathering the HLW glasses indicates that the formation of secondary phases can alter the glass reaction affinity, allowing the reaction to continue under high elemental concentration levels in solution. Studies over a range of temperatures suggest that the same mechanistic processes occur at all temperatures, but that the importance of a process or rate-controlling step may vary with temperature. Stable secondary phases which contain radionuclides form as the glass reacts. These phases may form on the surface of the glass or may form throughout the altered layer due to restructuring of the surface alteration layers.

- The importance of glass weathering to the release of radionuclides from glass has been examined in aqueous corrosion tests where statically weathered glass has been exposed to both batch (MCC-1 type) or dynamic (drip) tests. Only a small fraction (few percent) of the sparingly soluble actinides (Pu and Am) in the corroded glass is found as solutes or colloids in the test solutions. However, most of the inventory of these radionuclides in the test solutions is often associated with colloids.

- 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.

4.0 FIELD TESTING AND MATERIALS INTERACTIONS

The corrosion of HLW glasses has been studied extensively in laboratories worldwide (see Sections 2 and 3). Experiments have also been conducted in various geological formations to provide evidence that our understanding of the corrosion of HLW glasses based on laboratory experiments is relevant to geologic disposal. Five major field tests that have been or are being conducted are reviewed in Section 4.1, and the extent of interaction of the waste form with various metals and packing materials is discussed in Section 4.2.

4.1 Field Testing

Field tests of waste glass corrosion are important because they allow for more realistic simulation of geometric scale, materials interaction, and mass transport effects than can usually be achieved in laboratory tests. Using field tests to study waste glass corrosion has a number of limitations. Field tests are more difficult to control than laboratory experiments, and the leachates are usually not available. Analysis of glass corrosion in these tests must, therefore, depend on surface analysis of the retrieved samples. In general, field tests do not provide the control of experimental variables that is required to fully interpret the results. Thus, the results may be of limited use in developing an understanding of waste glass dissolution. On the other hand, field tests are important for providing evidence that the understanding gained from laboratory experiments is relevant to waste glass corrosion and weathering in underground environments and for providing information (often qualitative or semiquantitative) on the interactions between waste glass and other materials.

The five major programs to study glass corrosion in a geologic setting are listed in Table 4-1. These programs are discussed briefly in Sections 4.1.1 through 4.1.5.

Table 4-1. Major Programs Studying Glass Durability in a Geological Setting

Country	Location	Geological Material
Canada	Chalk River	Sand
England	Ballidon	Limestone
Belgium	Mol	Clay
Sweden	Stripa	Granite
U.S.	WIPP	Salt

4.1.1 Chalk River Program

In 1958, 25 nepheline syenite-based glass (aluminosilicate) hemispheres containing radioactive ^{90}Sr, ^{106}Ru, ^{137}Cs, and ^{144}Ce were buried below the water table in sandy soil at the Chalk River Nuclear Laboratories [WALTON-1981]. These glass samples were exposed to flowing groundwater at 6°C. In 1960, 25 additional hemispheres of a slightly less durable nepheline syenite-based glass were buried. Migration of the radionuclides Cs and Sr was monitored for up to 20 years [MERRITT-1967, LYON-1985]. A program is in progress to recover and examine some of the buried glass samples. Because this study involved aluminosilicate glass instead of borosilicate glass and the glass was emplaced directly into flowing groundwater, the results are difficult to compare with the other four field tests discussed below.

4.1.2 Stripa Mine Program

A joint project initiated in 1982 involved participation by the University of Florida, the Savannah River Laboratory, and the Swedish Nuclear Fuels Safety Division of the Nuclear Fuel Supply Company.[4] The purpose was to evaluate the burial of glasses in the Stripa mine, an experimental granite field laboratory in central Sweden. Two glass configurations were used: (1) minicans (stainless steel rings in which glass was cast) and (2) pineapple slices, which had a central hole through which a heater was inserted (Figs. 4-1 and 4-2). Temperatures of 8 to 10°C (ambient) and 90°C were evaluated. Assemblies of glass samples were prepared by stacking them together with granite, compacted bentonite, and metal rings to provide different types of interfaces for evaluation.

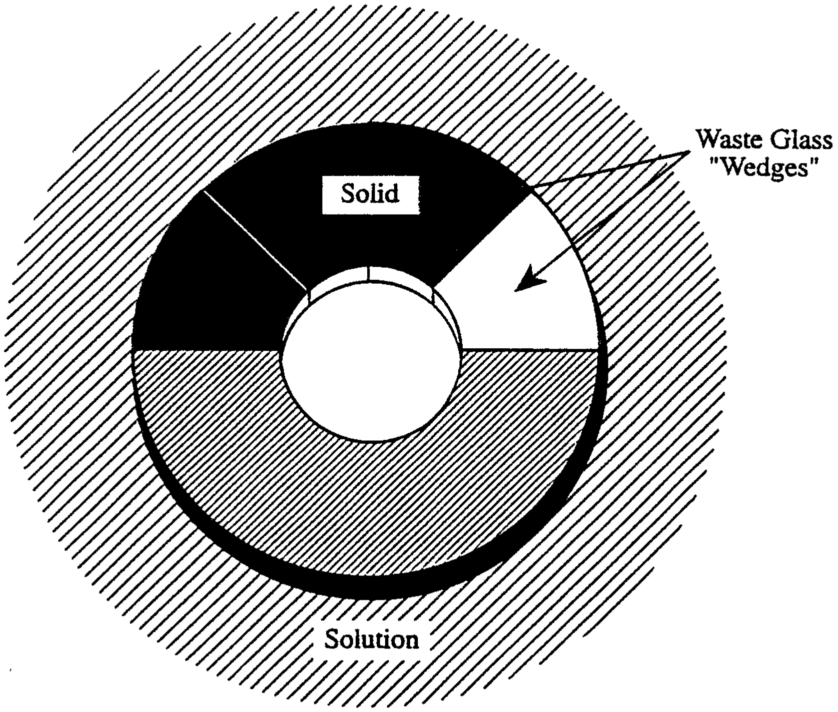

Fig. 4-1. A "Pineapple Slice" Glass Test Sample Shape (adapted from [COVINGTON-1989]).

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[4] Burial experiments in Stripa involving borosilicate glasses were initiated by the Swedish Nuclear Fuels Safety Division prior to this joint project.

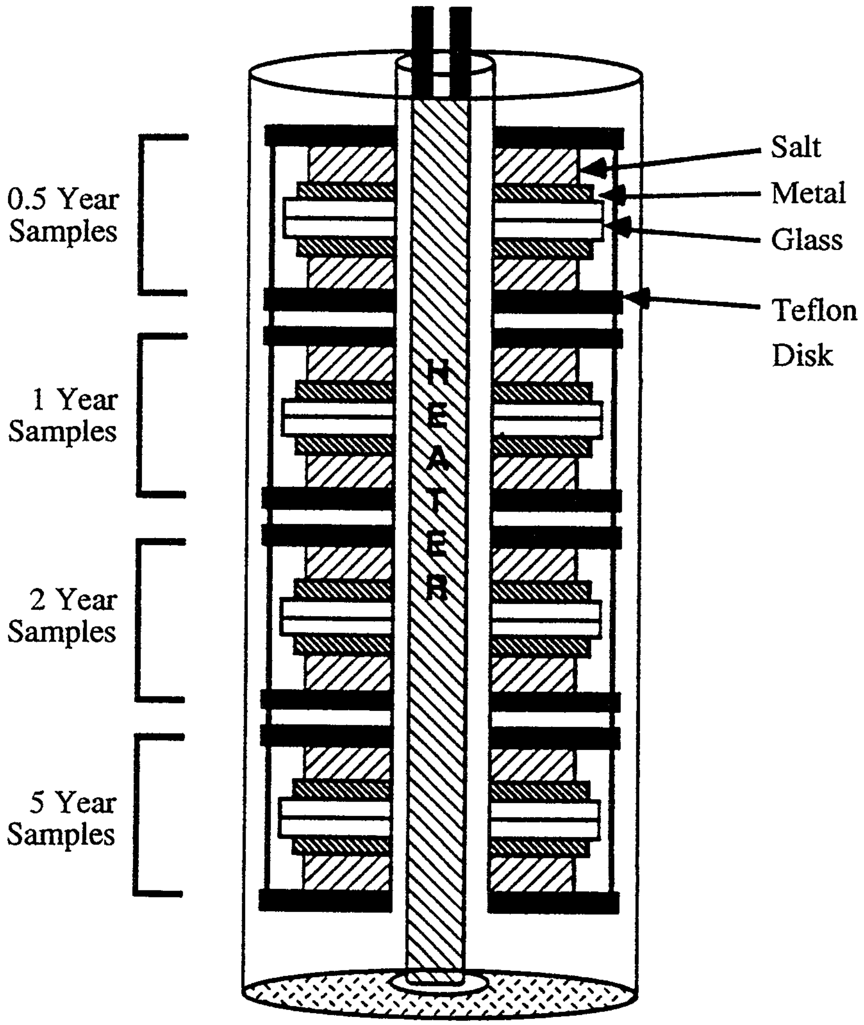

Fig. 4-2. An MIIT Sample Assembly for WIPP (adapted from [COVINGTON-1989]); Similar Assemblies Were Used for the Stripa Experiments.

Clark et al. [CLARK-1989] correlated the leaching results of laboratory and Stripa tests for an SRL 165 glass at 90°C by analyzing the reacted surface layers with various surface analysis techniques. They concluded that the leaching mechanisms appeared to be similar, although slower, in the Stripa granite. Initially, the glasses corroded rapidly; thereafter, the corrosion rate slowed considerably once silica saturation was reached.

Werme et al. [WERME-1985] summarized some of the results of testing two Swedish ABS glasses for one year in the Stripa mine. Glass/glass, glass/granite, and glass/bentonite interactions were evaluated. Basically, field testing confirmed the results of laboratory testing. The investigators examined differences in surface composition (Na^+, Cs^+, K^+, and Li^+ normalized to Si^{4+}) as measured by SIMS and confirmed the higher durability of ABS 41 glass compared with ABS 39 glass, as originally measured in the laboratory, based on the greater depletion depths of the alkali metals in the ABS39 glass. Contact of bentonite with either glass resulted in significantly increased depth of attack (about 4-fold) compared to glass without bentonite contact. Contact with granite during the first three months of burial resulted in an initially rapid attack, which was explained as being due to an ion-exchange process, but thereafter attack was less than that of glass in contact with other glass samples. This result was consistent with the results of Clark et al. [CLARK-1984] and Zhu et al. [ZHU-1985], who studied the leaching at 90°C of SRL 165-simulated waste glass buried in the Stripa mine. The effect from contact of the glass with granite was minimal.

4.1.3 Hades Facility Test Program

In 1987, in-situ corrosion testing was begun of various borosilicate waste glasses in Boom clay at the Hades facility in Mol, Belgium. Various components of the potential engineered barrier system were tested, such as the waste form, canister, container materials, and other possible construction materials such as concrete. Various waste glasses, container and canister materials, and structural components were installed in the clay. Tests were conducted at 90 and 170°C for periods up to five years. Some samples were in direct contact with clay, and others were contacted by humid air that had been passed through the clay. Results from these tests are discussed in Section 4.2.3.2.

4.1.4 Ballidon Limestone Program

The Ballidon Limestone program was begun in 1970 [NEWTON-1985c] by the British Glass Industry Research Association and expanded in 1986 into a joint effort between the University of Sheffield and Savannah River Laboratory. A total of 46 SRS waste glasses and natural glass analogues were placed in Ballidon limestone for one, two, five, and sixteen years. The sample type used was the pineapple slices and included SRL 131 TDS and SRL 165 TDS glasses [WICKS-1986]. Tests were conducted at ambient temperature one meter below the limestone surface. Samples were analyzed for reaction depths and reaction layer compositions determined by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), wide angle X-ray diffraction, SIMS, and fourier transform infrared reflectance microscopy (FT-IRRS). After two years of testing, interaction zones on the surfaces of the glass samples were very thin, less than 1 μm thick [NAMBOODRI-1991]. Results indicated that the test glasses performed in a similar manner as glasses tested in other underground environments. The shallower leaching depth observed with limestone was thought to be the result of testing under ambient temperature conditions, compared with testing at 90°C in some of the other environments.

4.1.5 MIIT Program at WIPP

In a program begun in 1986, about 2000 samples of simulated waste glasses and potential package components were buried in the salt formation at the WIPP in Carlsbad, New Mexico [WICKS-1986, -1992]. These samples were to be evaluated after exposure for a period of up to five years in a study termed the Materials Interface Interactions Tests (MIIT). The program was managed by Savannah River Laboratory and Sandia National Laboratory, and eight countries--Belgium, Canada, France, Germany, Japan, Sweden, the United Kingdom, and the United States--were involved. A total of 15 distinct waste glass and waste form systems were tested (see Fig. 2-1 and Appendix A in Volume I for the glass compositions). Waste glass samples were fabricated in the shape of pineapple slices that were polished on one side. Proposed package components were made in a similar configuration. Slices of glasses, metal components, and geologic samples were stacked onto heater elements for testing. A total of 50 assemblies of pineapple slices were created in seven different stacking arrangements and tested in 50 underground boreholes. Of these 50 boreholes, 46 were filled with brine and 4 were dry. A temperature of 90°C was maintained, and samples were removed for evaluation after six months and one, two, and five years. The tests were designed to allow solution data to be obtained from the brine boreholes, and the modular design of the test assemblies allowed surface analysis of samples exhumed after six months, one year, two years, and five years. Although the analysis of the retrieved glass samples is still in progress, some of the findings from the detailed studies of the surface alteration layers, using a variety of surface analytical techniques, are summarized below [WICKS-1993].

Figure 3-1b in Volume I illustrates the SIMS elemental profiles that have been observed. Although the elemental profiles represent continuous curves, the major characteristics can be described in terms of five "layers". In addition to two outermost precipitation layers (designated α_0 and α_1), three layers were identified in the "reaction zone" (designated β_0, β_1, and β_2) which can be considered to represent progressive stages in the corrosion of the underlying glass. The outermost β_0 layer is characterized by intrusion of the brine constituents and depletion, with flat concentration profiles, for the glass components. Because the glass network has presumably been extensively hydrolyzed in this layer, it corresponds to the gel layer discussed elsewhere throughout this document. Underlying this layer are the "Gradient" and "Diffusion" zones (designated β_1 and β_2, respectively) wherein the glass network is progressively less hydrolyzed as the underlying unreacted glass is approached. These layers correspond to the Diffusion or Reaction zone discussed elsewhere throughout this document. Based on the surface layer structure, it appears that the corrosion processes for the glass samples under field conditions are similar to those observed in laboratory tests. After five years of testing, 12 of the 16 glass compositions had reaction depths between 0.4 and 8 μm (which corresponds to a corrosion rate range of approximately 6×10^{-4} to 1.2×10^{-2} g/m^2/d) [LODDING-1994].

Brine leachates from selected MIIT boreholes were analyzed using ICP-MS to determine Li, Zr, La, and Eu which were added to the glass. The La and Eu dopants were intended to simulate +3 and +4 actinides. Based on the leachate data, the estimated upper limit on the leach rate for La was 3.5×10^{-4} g/m^2/d and for Eu was 3.0×10^{-4} g/m^2/d [WICKS-1994].

The five year glass/metal (304L, Pb, A216 carbon steel, and Ti code 12) interface interaction data showed only small effects when compared to glass/glass interfaces [CLARK-1994]. SEM/EDX analysis of the SRL-165 glass indicated that the rate of corrosion observed between years 3 and 5 was greater than that observed during the first two years [MACEDO-1994].

Clark et al. [CLARK-1992a] summarized the five-year results of metal and overpack interactions with the waste form from the WIPP/MIIT burial studies as follows:

> In contrast to earlier shorter term testing which showed that the presence of carbon steel appeared to increase waste form leaching and the presence of lead decreased it, the five-year results from WIPP show that the presence of 304L stainless steel, lead, A216 carbon steel, and Ticode 12 did not significantly affect the performance of SRL 165/TDS glass. The total extent of interaction was small.

4.2 Materials Interactions

Some possible materials interactions in a repository are:

1. Glass/canister (304L stainless steel);
2. Glass/container material (e.g., carbon steel, Ti, Pb, others); and
3. Glass/packing material(s).

Materials interactions that have been observed are discussed in more detail in Sections 4.2.1 through 4.2.3.

4.2.1 Interaction with Stainless Steel

Because the waste form will be poured into stainless steel canisters, the interaction between the waste form and the canister is of interest. Austenitic stainless steel is the canister material designated by the WAPS [WAPS-1993]. Both the DWPF and WVDP plan to use 304L stainless steel. Barkatt et al. [BARKATT-1983b] studied the short-term leaching in deionized water at 70°C of powdered (-42 +60 mesh) borosilicate waste glasses (PNL 76-68 and SRL TDS 131) that were mixed with powdered stainless steel. The leachant was changed at specific intervals. The normalized release rate of eight different elements, including B and Na, was measured. For very short leaching times (six days) and coarse stainless steel (coarser than the glass), the presence of stainless steel decreased the leaching of the waste glass. For longer leaching times and fine stainless steel, the presence of stainless steel had no significant effect on the leaching.

Zhu et al. [ZHU-1985] studied the alteration of glass contacting stainless steel in a pineapple slice configuration at 90°C in Stripa granite for one year. The depth of attack measured with FT-IRRS showed that the presence of stainless steel had no effect on glass corrosion. Burns et al. [BURNS-1986] studied the leaching of SRL 131/TDS waste glass in contact with stainless steel at 90°C for 28 days in either deionized water or simulated basaltic groundwater, using an MCC-1 type test. The normalized release of B indicated no significant effect of the stainless steel for either leachant. Covington et al. [COVINGTON-1989] studied the interaction between glass and 304L stainless steel after up to two years of testing in WIPP at 90°C using SEM/EDS. They found no significant effect on glass corrosion resulting from the presence of stainless steel. In a review article, Bibler [BIBLER-1987] concluded that the presence of 304L stainless steel in contact with the waste form during leaching did not appear to affect the corrosion behavior under conditions simulating a tuff repository environment.

Tsukamoto et al. [TSUKAMOTO-1988] studied the leaching of Am-241 from radioactive JSS-A glass at 90°C in distilled water. Leaching of Am-241 was higher in the presence of stainless steel reaction products than when these products were absent. This result was explained on the basis of an increased glass corrosion rate due to reaction of silica in solution with the metal reaction products. Precipitation from solution of the reaction products decreased the silica concentration and thereby increased the dissolution affinity. Bibler [BIBLER-1987] summarized glass/stainless steel interactions for various repositories as follows: nonsensitized stainless steel has no significant effect on glass corrosion whereas sensitized stainless steel may lead to limited, localized increased leaching.

Bates et al. [BATES-1988b] investigated stainless steel/SRL 165 glass interface reactions at 90°C with tuff-containing water in both stagnant and flowing conditions in the laboratory. When the metal was given a sensitization treatment (24 hours at 550°C), the glass reaction with water tended to increase for 52-week tests in which the same water was used throughout the test but not for shorter or longer test periods with a continuous change in the water solution. Increased glass reaction occurred only for glass in contact with metal and only for some sensitized metal. Bates et al. [BATES-1990d] also reported the results of laboratory tests conducted for up to 250 weeks with sensitized 304L stainless steel (24 hours at 550°C). The effects of the sensitized stainless steel on the glass corrosion rate were generally small with the maximum increase observed in the corrosion rate being less than a factor of two. The sensitization heat treatment of 24 hours at 550°C studied by Bates [BATES-1988b] would not be expected to be approached by any canister during cooldown nor in any anticipated storage, transportation, or geologic disposal situation.

4.2.2 Interaction with Metals Other than Stainless Steel

Although 304L stainless steel has been selected as the canister material for at least DWPF and WVDP, the material for the waste package container has not been selected. Possibilities include mild carbon steel, stainless steel, Cu, Ti, Pb, and others.

Barkatt et al. [BARKATT-1983b] studied corrosion in deionized water at 70°C of powdered SRL 131 TDS and PNL 76-68 waste glasses mixed with Pb shot. The leachants were completely replaced at specified intervals. The initial leach rates of eight different elements in SRL 131 TDS glass were depressed by the presence of Pb for test times of up to 15 days, but for longer times the leach rates of these elements were unaffected, except for Si and Fe. This initial beneficial effect of Pb was explained by the formation of a protective lead silicate layer on the glass surface, which became unstable and nonprotective after longer leach periods. For the PNL 76-68 glass, the lead silicate layer on the glass surface continued to retard the leaching of all eight elements monitored for the length of the experiment (86 days).

Barkatt et al. [BARKATT-1983b] also studied the effect of the presence of either powdered Al or alumina on the dissolution of PNL 76-68 waste glass, which is free of alumina. Initially, the presence of alumina or Al depressed the normalized release of Si by a factor of 80 and the normalized releases of B, alkalis, and alkaline earths by a factor of six. By the end of the 100-day test, normalized releases were still reduced by a factor of three.

Burns et al. [BURNS-1986] studied the normalized release of B from an SRL 131 TDS waste glass in contact with various metals in an MCC-1 test at 90°C for 28 days under oxidizing conditions using either deionized water or simulated basaltic groundwater. Metals studied other than stainless steel were A516 low carbon steel, 409 and 430 ferritic steels, E-brite, Ticode 12, Inconel 600, and Pb. The normalized release of B from SRL 131 TDS glass is shown in Fig. 4-3; only A516 steel and Pb had a significant effect on glass leaching. The presence of A516 steel increased the B release by a factor of about two, whereas the presence of Pb decreased B release by about a factor of 10. The presence of Pb was thought to cause the formation of a protective layer on the surface of the glass.

Werme et al. [WERME-1982] studied the corrosion of ABS glasses in the presence of Pb, Cu, and Ti in the Stripa granite mine under reducing conditions and found little effect of these metals. Barkatt et al. [BARKATT-1983b] studied the corrosion (at 70°C) of three different SRL powdered glasses in the presence of Pb shot, with the leachate changed at regular intervals, and reported that the presence of Pb caused glass leaching to decrease.

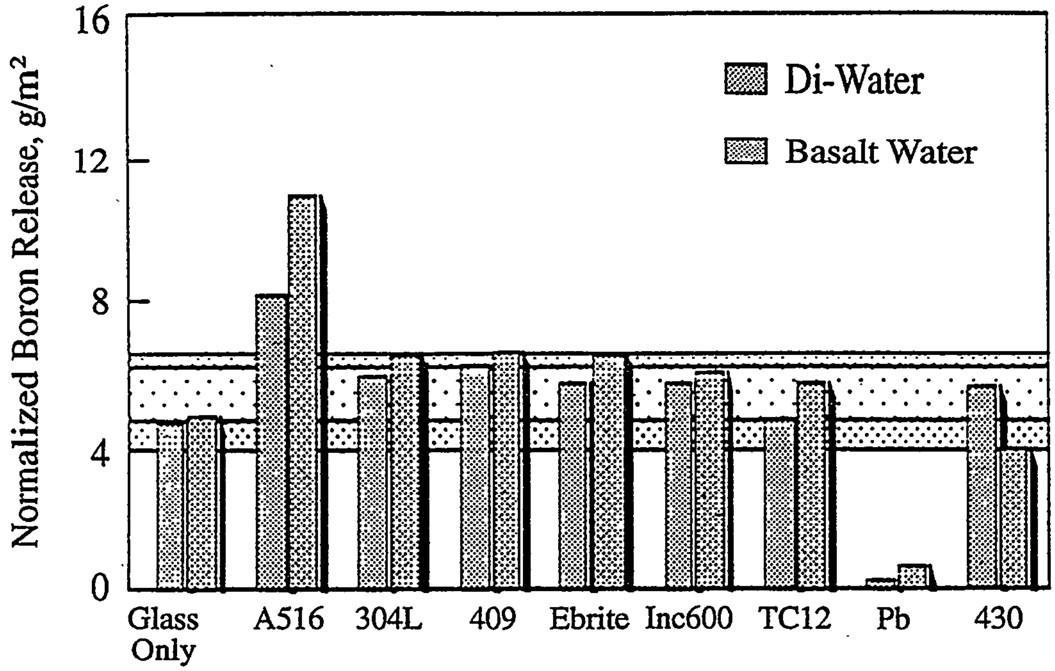

Fig. 4-3. Leaching of SRL 131 TDS Waste Glass in the Presence of Various Metals in Deionized Water or Basalt Leachant (adapted from [BURNS-1986]).

Under certain conditions, the presence of carbon steel appears to increase glass leaching via the "iron-pumping mechanism" first proposed by McVay and Buckwalter [McVAY-1983] and reinforced by Jantzen [JANTZEN-1984b]. The mechanism involves scavenging silica from the solution by reaction with Fe^{2+} to form an iron silicate precipitate. The removal of Si from the leachate acts as the driving force (or pump) for further dissolution of the glass. This explanation is consistent with the role of Si in solution as controlling the rate of glass dissolution (see Volume I, Section 3.2).

Covington and Wicks [COVINGTON-1989] studied the effects of interactions between glass and Ticode-12, Pb, and A216 carbon steel in WIPP after up to two years of testing at 90°C. No significant effect on glass corrosion resulted from the presence of these metals. The presence of Pb was either neutral or decreased glass leaching slightly; the other metals did not have a significant effect. Clark et al. [CLARK-1992a] summarized the results of testing 304L stainless steel, Pb, A216 carbon steel, and Ticode-12 for five years in WIPP by concluding that the presence of these metals had no significant effect on the leaching of SRL 165 TDS glass.

4.2.3 Interaction with Packing Materials

The interactions of waste glass with crushed repository rock and swelling clays are discussed in Sections 4.2.3.1 and 4.2.3.2, respectively. The interactions involved are associated with the effects of these materials on the Si concentration in the leachate.

4.2.3.1 Repository Rock

Many investigators have found that the groundwaters of the various potential repositories are less corrosive than is either distilled or deionized water. Strachan [STRACHAN-1982] studied the change in composition of different leachants in an MCC-1 test of PNL 76-68 glass after up to one year of leaching. He found that the concentration of Si in solution reached the same final value at 90°C in either distilled water or silicate water. However, because the silicate water initially contained a higher level of Si, less Si was leached from the glass. Work at the Lawrence Livermore National Laboratory has shown that using J-13 groundwater from Yucca Mountain to which tuff rock has been added decreases the corrosion of PNL 76-68 glass at 90°C [OVERSBY-1984]. This effect was attributed to the increased silica in solution from dissolution of the tuff, which decreases the rate of dissolution of silica from the waste glass (see Sections 2.3 and Volume I, Section 3.3.2.2). The review by Bibler et al. [BIBLER-1988a] also reported that when powdered tuff is present in the leaching solution, the presence of tuff lowers the corrosion rate compared with that of the unaltered leachant.

Werme et al. [WERME-1985] studied the leaching of ABS 39 and ABS 41 glasses in contact with granite slices in the Stripa mine (see Section 4.1.2). During the first three months of burial, attack on the glass was high due to an ion-exchange process, but thereafter attack was lower than that of glass in contact with other glass samples. Clark et al. [CLARK-1984] and Zhu et al. [ZHU-1985] studied the corrosion at 90°C of SRL simulated waste glasses buried in the granite of the Stripa mine. The effect of contact of the glass with granite was minimal.

The presence of silica in the leachant can slow the rate of dissolution. For example, Lanza [LANZA-1982] reported that for a generic waste glass containing 20 wt.% simulated waste oxides with distilled water as the leachant, there was a short initial stage of direct dissolution in which mass loss increased linearly with time followed by a slower stage in which the mass loss increased with the square root of time. With a solution saturated in silica, the initial more rapid stage was absent. Bibler et al. [BIBLER-1985] reported that the presence of tuff in the leachant significantly decreased the concentrations of leached species from a generic SRL waste glass. The presence of tuff rock was reported to have buffered the pH change of the solution. Bibler et al. [BIBLER-1987] studied the leaching of SRL 165 glass in an MCC-1 test using simulated groundwater. They reported that normalized mass losses for Si were low because the groundwater was already partially saturated with Si.

In contrast to the results of most researchers in this area, Hermansson et al. [HERMANSSON-1983] studied the leaching of ABS 39 and ABS 41 glasses in various leachants and reported that the normalized mass loss of Si for both glasses was higher in silicate water than in distilled water for the first 91 days of exposure. After 182 days of exposure of ABS 39 glass, the weight loss in all leachants was the same. Oversby [OVERSBY-1984] reported that for SRL 165 frit leached in J-13 water with or without tuff present, the largest release of B occurred in J-13 water without added tuff rock. Barkatt et al. [BARKATT-1991] studied corrosion of multicomponent borosilicate glasses at 90°C using a partial-replenishment technique. The leachants tested included deionized water, pH buffered solution, and NaOH; brief periods of accelerated corrosion were observed in deionized water that were not observed in buffered leachants.

Bibler [BIBLER-1987] in a review paper summarizing various repository conditions concluded that groundwaters from tuff, salt, basalt, or granite were less corrosive to borosilicate waste glasses than was distilled water, although the difference was never more than a factor of two. The presence of tuff, basalt, or granite buffered the pH of the leaching solution.

4.2.3.2 Clay

Bentonite clay has received consideration as a component of packing material because of its low moisture permeability. Godon and Vernaz [GODON-1990] reported that the chemical compositions of clays reflect the environments with which they are in contact. Smectite, for example, is stable at lower pH values (7.5 to 8.5 at 90°C) and reaches equilibrium at low Si concentrations (20 ppm at 90°C). At Si solution concentrations lower than 20 ppm, smectite contributes Si to solution where, at higher Si concentrations, smectite removes Si from solution. When other bentonites, stable at higher pH (9 to 10), are placed in pure water, they reach equilibrium at moderate Si concentrations of 80 to 90 ppm [VAN ISEGHEM-1990b]. For these reasons, the chemical characteristics of the clay affect the leaching environment and the degree of attack on the waste form. Lanza and Ronsecco [LANZA-1982] reported that distilled water containing montmorillonite clay had a higher pH than water containing bentonite. Van Iseghem et al. [VAN ISEGHEM-1990b] reported that the mass loss (Cs, Sr, Pu, Am) from SON 68 and SM 513 glasses was four times higher in dilute Boom clay solution than in deionized water.

Tsukamoto et al. [TSUKAMOTO-1988] studied the amount of Am-241 in a leachate of distilled water containing bentonite that was reacted at 90°C with radioactive JSS-A glass. They reported that Am-241, present in the leachate in colloidal form, was strongly adsorbed by the bentonite in the leachate, thereby decreasing the mobility of Am.

Clark et al. [CLARK-1984] and Zhu et al. [ZHU-1985] studied corrosion of SRL glasses and Hench et al. [HENCH-1982b] and Werme et al. [WERME-1982] studied the corrosion of French AVH glasses, all of which were in contact with bentonite while buried in granite of the Stripa mine at 90°C. For SRL glasses buried for up to three months, Clark et al. [CLARK-1984] reported a much thicker reacted surface layer on glasses in contact with bentonite than on glasses in contact with other test materials (stainless steel, granite, Pb). Such contact between these glasses and bentonite resulted in increased attack on the glasses. Hench et al. [HENCH-1982b] reported that the degrading effect of bentonite was accelerated at higher bentonite/water ratios, such as would be present in an unsaturated repository. Thus, the use of clay as a packing material to retard the migration of radionuclides must be evaluated against the potential for increased attack on the waste form by the presence of the clay.

4.3 Summary

- In general, observations from field tests indicate that the corrosion behavior under field test conditions is similar to that observed in laboratory tests. Clark et al. [CLARK-1992b] summarized the results of fielding testing in granite, salt, and limestone as follows:
    - The total extent of glass interaction was small after up to five years of exposure.
    - Corrosion of SRL waste glasses was similar in salt and granite (both at 90°C) but much less in limestone at ambient conditions. The limestone results were comparable to the granite results at ambient temperature.
    - Selective dissolution appears to have been the primary leaching mechanism.

- Vernaz and Godon [VERNAZ-1988b] reported that a significant difference in the results of the WIPP testing compared with other field testing was the formation of a Mg-Si phase as a result of reaction between Mg from the salt with Si in solution. Formation of this Mg-Si phase could prevent silica in solution from reaching saturation, thereby allowing the corrosion to continue at an appreciable rate.

- Interactions with metal components of the engineered barrier system in a repository (such as carbon steel or lead) may promote or inhibit glass corrosion depending on whether these interactions promote precipitation of silicate minerals or promote formation of protective layers on the glass surface. Interactions with bentonite clay in packing materials may increase waste glass corrosion.

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5.0 OBSERVATIONS FROM NATURAL GLASSES

One of the tools that has been suggested for solving the problem of the validation of models for the long-term corrosion of waste glass are studies of natural analogues. A "natural analogue" refers to a naturally occurring system or material that can give information about an engineered system of interest [EWING-1991; CHAPMAN-1984, -1986; PETIT-1992]. For the purposes of this discussion, use of the term will be limited to basalt glasses, rhyolite glasses (obsidian), and tektites.[5] Such materials are found throughout the natural environment, having been exposed to a range of ambient conditions of temperature and water contact. The ages of natural analogues studied range typically from thousands to millions of years. The excellent durability demonstrated by natural glass in unengineered settings is desired for HLW glasses in a repository, but to relate these durabilities requires a technically valid approach. Several reviews of the use of natural glass analogues have been presented recently [PEARCY-1991; MCKENZIE-1990].

Natural analogue systems can be divided into two general groups: whole-system analogues and process-oriented analogues [CHAPMAN-1986]. Process-oriented analogues are natural systems with one or more of the chemical processes found in the system of interest [CHAPMAN-1986; EWING-1987]. Whole-system analogues have many or all of the processes found in an engineered system, but these are scarce [CHAPMAN-1986]. Investigation of suitable analogues can provide evidence that the glass corrosion processes observed in short-term laboratory and field tests are the same processes that will occur in long-term corrosion. In addition, if the rates of these processes and the history of the corroding environment can be established, these rates can be used to validate predictive models.

5.1 Basalt Glasses

Natural basalt glasses are frequently cited as appropriate natural analogues for studying HLW glass alteration in a repository. The known ages of basalt glasses typically range up to millions of years [ALLEN-1982; EWING-1978; BYERS-1987; KEITH-1985; CROVISIER-1992]. Among the justifications for the analogy to HLW glasses are similarities in composition and similarities in reaction conditions.

Borosilicate glasses with compositions similar to HLW glasses do not occur naturally. Among the natural glasses available for study, basalt glasses are the closest in composition to the HLW glasses; the similarities are strongest with respect to silica content, as shown in Table 5-1. Basalt glasses typically contain only trace amounts of B and Li and significantly less alkali metals than HLW glasses.

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[5] Basalt glasses are volcanic glasses with relatively low amounts of SiO_2 (approximately <50 wt.%), and rhyolite glasses are volcanic glasses with relatively high amounts of SiO_2 (approximately >50 wt.%). Impact glasses, including tektites, are glasses that form as a result of extraterrestrial bodies impacting the earth's surface. Tektites are similar in silica content to rhyolite glasses, but have lesser amounts of Na, K, and water and greater amounts of Fe. These descriptions are greatly simplified.

Table 5-1. Chemical Analyses of Natural Glasses (wt.%)

Oxide	Indochina Tektite	Rhyolite Glass 4-1	Basalt Glass
SiO_2	74.4	74.9	50.7
Al_2O_3	12.17	14.20	11.7
Na_2O	1.32	4.68	4.5
K_2O	2.61	4.59	0.7
FeO	--	0.49	--
Fe_2O_3	5.58	0.29	13.1
MnO	0.11	0.03	0.4
MgO	1.85	0.02	6.7
CaO	1.52	0.53	10.6
TiO_2	0.76	0.04	1.9
B_2O_3	--	--	--
Li_2O	--	--	--
NiO	--	--	--
ZrO_2	--	--	--
H_2O+	0.01	0.87	0.2
Total	100.34	100.13	100.5

H_2O+ refers to the total intrinsic water content.

Basalt glasses are also considered appropriate analogues for HLW glasses because of the similarities in reaction conditions expected in a repository and those commonly found for basalt glass exposures. Basalt glasses are known to have existed on earth under three general sets of conditions: (1) submarine exposures, where the reaction solution contains relatively large amounts of alkali salt compared with meteoric (fresh) water; (2) subaerial exposures, where the glass is constantly or intermittently exposed to meteoric (fresh) water; and (3) some combination of submarine and subaerial exposures. These cases constitute conditions that likely bracket the expected and unexpected conditions that HLW glasses will experience in a repository (i.e., S/V ratios ranging from very large to very small; contacting aqueous phase ranging in composition from concentrated to dilute; and periods of time bounding the likely lifetime of a repository). The results reported by Byers et al. [BYERS-1987] indicate that the alteration of basalt glasses in subaerially exposed conditions can be reproduced in laboratory vapor experiments.

Alteration of basalt glasses with water and its relationship to possible HLW glass corrosion has been the subject of a number of studies [e.g., ALLEN-1982; BYERS-1987; CROVISIER-1987, -1992; JERCINOVIC-1987; EWING-1987]. Naturally altered basalt glasses commonly form a poorly crystalline alteration product called palagonite. Palagonites are widely variable in composition and appearance and are difficult to characterize. Several studies have observed that the composition of the palagonite (alteration layer) on naturally altered basalt glasses is almost identical to intergranular clay material associated with the same glass [CROVISIER-1992]. Palagonite is the natural analogue to the gel layers that develop on borosilicate glasses (see Section 2.1 for a description of gel layers.) A second common type of alteration product associated with naturally altered basalt glass is secondary minerals. In some cases, no secondary mineral formation is observed [GISLASON-1987]. Many natural analogue studies have found that the secondary minerals that form on basalt glasses are the same secondary phases that form on altered HLW glasses [JERCINOVIC-1987; BYERS-1987; LUTZE-1987; CROVISIER-1992]. These minerals can include, but are not restricted to, smectite clays, analcime, phillipsite, thomsonite, chabazite, erionite, garronite, calcium silicates (gyrolite, tobermorite), and carbonate minerals. The variability in composition of the alteration mineral assemblage is a strong function of the alteration conditions. The similarities between the palagonite layers on natural basalt glasses and the gel and secondary precipitate phases observed on HLW glasses provide evidence that the reaction paths observed in laboratory studies are similar to those that occur over long time periods.

Basalt glasses experimentally altered in vapor atmospheres have been shown to more closely resemble naturally altered basalt glasses than basalt glasses experimentally altered in leaching tests with respect to the alteration minerals formed [BYERS-1987]. The minerals formed in vapor atmospheres included smectite clay, analcime, thomsonite, phillipsite, gyrolite, garronite, and aragonite. Furthermore, HLW glasses and basalt glasses experimentally altered in vapor atmospheres formed many of the same alteration phases, including smectite clay, analcime, and gyrolite. From these results, Byers et al. concluded that vapor hydration experiments more closely reproduced the natural alteration of subaerially exposed basalt glass than did leaching experiments at the same temperature [BYERS-1987].

Submarine and subglacial basalt glasses from the United States, Iceland, and Antarctica were studied with optical and scanning electron microscopy [ALLEN-1982]. These glasses were studied because of their long-term stability in natural environments. The glasses ranged in age from 0.6 to 22 million years old, and their natural environments were estimated to have included intermittent exposure to water and temperatures near 0°C. Alteration products on the glasses included Fe-rich cryptocrystalline clays (palagonite) that were observed to be similar in appearance and cation depletion to gel layers found on leached HLW glasses [ALLEN-1982]. The following conclusions are based on these studies: (1) surface alteration of HLW glass would occur rapidly (approximately tens of microns in the first year) when the glass was exposed to water; (2) the surface layer would protect the underlying glass from further reaction for millions of years; and (3) the surface layer (specifically zeolites) would sequester a portion of the released radionuclides (see Section 2.7.2).

A study of basaltic glasses was conducted [JERCINOVIC-1987] to identify the long-term corrosion products, to determine the long-term corrosion rate (including the effect of silica concentration), and to examine elemental mass balance (i.e., elemental loss to and pickup from the corrosion environment). The samples examined were obtained from subglacial-volcanic deposits, submarine deposits, and the sea floor. In their natural environments, these samples had been exposed to glacial melt, meteoric, and sea water in configurations that ranged from closed to open systems. The surface alteration layers (palagonite) were examined in detail. They were found to contain both amorphous (hydrous silica and metal oxide gels) and crystalline phases (principally smectite-type clays) and had a structure that indicated that they did not represent a mass transport barrier. Examination of the surface layers produced under closed system conditions (i.e., in tight cracks or pores where the contacting water was stagnant or very slowly refreshed) indicated that precipitation of silica-containing phases can result in increased corrosion of the glass based on the observed surface alteration layer thickness. Similar to laboratory studies, the flow rate (or refreshment rate) of the contacting water and the exposed glass surface area were found to be critical parameters. A significant observation in this connection was that, even in tight fractures, prominent alteration layers were observed (see discussion of waste glass surface area in Section 2.3.5). The long-term stability was found to be enhanced under conditions where the silica concentrations in solution were increased. Although it is difficult to determine the corrosion rates for natural samples, the evidence was consistent with a corrosion rate characterized by an "initial rate" in silica-undersaturated environments and a "long-term rate" in silica-saturated environments. In general, it was concluded from this study that there is considerable agreement between corrosion phenomena observed in the laboratory with borosilicate glasses and those observed for natural basaltic glasses of great age.

Japanese basalt glasses between 280 and 2800 years old were studied in conjunction with laboratory experiments with HLW glasses [YASUHISA-1990]. This study concluded that the alteration products found on naturally altered basalt glasses (smectite clays) and on laboratory-altered HLW glasses were grossly similar in appearance and composition, which is further evidence that the long-term processes are similar to those that occur in laboratory studies. This study also found that alteration rates in groundwater for basalt glasses decreased with increasing silica content in groundwater, which suggests that the dissolution step--which controls the rate of corrosion in laboratory studies--may also be important in controlling long-term corrosion rates.

A microprobe study of the secondary minerals that formed during Hawaiian basalt glass alteration in fresh water was performed for samples 12,000 to 28,000 years old [COWAN-1986, -1989]. The zeolite and palagonite phases found on the naturally altered glass were reported as being almost identical to those found on experimentally leached borosilicate waste glasses.

5.2 Rhyolite Glasses

Natural rhyolite glasses (obsidians) are less frequently cited as appropriate natural analogues for studying HLW glass alteration in a repository. Obsidians typically contain approximately 20 wt.% more silica than basalt or HLW glasses, but have similar amounts of alkali metals compared with waste glasses (see Table 5-2). Natural obsidians are found under reaction conditions less diverse than those found for basalt glasses. Studies of obsidian as a natural analogue have generally emphasized a whole-system approach [KARKHANIS-1980; DICKIN-1981; MAGONTHIER-1992].

Karkhanis et al. [KARKHANIS-1980] leached discs of quaternary rhyolite glass (up to 2×10^6 years old) in distilled water at 100, 200 or 300°C for up to 7 days. The rates of elemental release were described as being consistent with stoichiometric network dissolution, and the temperature dependence of the reaction was characterized by an activation energy of approximately 50 kJ/mol. Large amounts of muscovite--a stable, hydrous, mica sheet silicate [$KAl_2(AlSi_3)O_{10}(OH)_2$]--had formed in altered glass. On the basis of leaching kinetics, the authors concluded that the rhyolite glass reaction mechanism observed in their experiments was different from the ion-exchange mechanism observed at 25°C in other experimental studies [WHITE-1980]. The 100°C leach rates were a factor of 2 to 10 times larger for a borosilicate glass than for rhyolite glass [KARKHANIS-1980].

Table 5-2. Results of Some Glass Natural Analogue Studies

Glass Type	Results/Conclusions	Reference
Basalt	Found that experimental hydration of basalt glass at high S/V (vapor hydration) more closely mirrored natural alteration than experimental hydration at low S/V (leaching tests). Vapor hydration test results indicated a close correspondence between alteration phases on basalt glasses and HLW glasses.	BYERS-1985, -1987
Basalt	Reviewed possible natural analogues dating back to 40 Ma, including volcanic glasses, tektites, and lunar glasses. Listed caveats for relating natural analogues to HLW glass durability projects.	EWING-1978
Basalt	Corrosion of natural glasses in submarine and subaerial environments was studied. The estimated minimum rate of corrosion at 5°C on the open ocean floor is 2.7 x 10^{-8} μm/d. Corrosion results in the formation of palagonite and smectite clays. These phases do not protect the glass from further corrosion.	JERCINOVIC-1987
Basalt	Corrosion of waste glass C-31 and Hawaiian basalt glass in NaCl brine at 200°C was compared. Nearly identical surface layers were found on each type of altered sample.	LUTZE-1985
Basalt	Studied natural glasses 280 to 2800 years old. Found alteration products similar to those on experimentally altered HLW glass. Natural alteration proceeds at 2 to 3 μm/1000 yr.	ARAI-1989; YUSA-1990
Basalt	Found that natural glasses (0.2 to 2.2 Ma) alter to initially form hydroxides, then phyllosilicates (including smectites), and finally zeolites. Geochemical simulations were able to reproduce this sequence by assuming that dissolution is network-hydrolysis controlled and chemical equilibrium exists through the solution. The palagonite is analogous to waste glass gel and adjusts its composition according to chemical variations of the solution.	CROVISIER-1992
Basalt	Determined that the natural rate of basalt glass alteration = 0.002 to 0.005 vol.%/yr, less than the experimentally predicted rate.	COWAN-1989

Table 5-2 (Contd.)

Glass Type	Results/Conclusions	Reference
Obsidian	Showed that glass alters to form alkali feldspar minerals.	DICKIN-1981
Obsidian	Showed that ion exchange is the long-term rate-controlling process. Glass alters to form Fe-rich aluminosilicate and $Al(OH)_3$.	MAGONTHIER-1992
Obsidian	Studied experimentally altered rhyolite glass and HLW glass in leach tests between 100 and 300°C. Leach rates at 100°C for both glasses were approximately 3.5×10^{-5} gm glass•cm^{-2}•d^{-1}.	KARKHANIS-1980
Obsidian	Water diffusion in natural high-silica glasses was isolated in vapor hydration tests between 100 and 230°C. The intrinsic water content of the glasses was shown to be an important parameter, affecting both the hydration rate constant and the activation energy.	MAZER-1992c
Tektite	Leach tests resulted in 23°C rates of 1.8×10^{-5} g•m^{-2}•d^{-1} and an activation energy of 79.6 ± 0.7 kJ/mol. Dissolution became stoichiometric very quickly. The good durability was attributed to the high silica content of the glass and its low alkali and low intrinsic water content.	BARKATT-1984b
Tektite	Leach tests with synthetic microtektite glass in seawater suggest that Mg in seawater suppresses leaching. A similar effect was noticed in experiments with HLW glass. Surface analyses of both glasses indicated that an Mg-rich layer has formed.	BARKATT-1989
Tektite	Background article describing tektites.	GLASS-1984
Tektite	Determined that water diffusion at 90°C in tektite = 0.01 $\mu m/d^{1/2}$.	MAZER-1992a
Tektite	Tektite corrosion between 50 and 90°C was studied by measuring the ingress of water into glass. The reaction was dominated by slow matrix dissolution. SRL 165 waste glass corrosion and surface layer formation was linear with the square root of time, which was attributed to ion exchange and matrix dissolution.	HAGEN-1988

In another study, natural high-silica rhyolite glass was altered under corrosion conditions at estimated temperatures of 400°C for 2 x 10^5 years. Analyses of the naturally altered glass indicated that it had formed an assemblage of alteration minerals that included epidote, $Ca_2(Al,Fe)_3Si_3O_{12}(OH)$, and stable alkali feldspars, $(Na,Ca,K)Al(Si,Al)_3O_8$ [DICKIN-1981]. A model for the alteration processes proposed that stable mineral formation on rhyolite glass was made possible by these minerals scavenging Ca^{2+}, Na^+, and Al^{3+} from the hydrothermal fluids. Karkhanis et al. [KARKHANIS-1980] suggested that, based on the results of this study of naturally altered rhyolite glass, a high-silica HLW glass would be more durable than borosilicate glass.

Molecular water diffusion has been identified as the rate-controlling reaction process in vapor atmosphere experiments with rhyolite glass [MAZER-1991b, -1992a, -1992c]. Water diffusion into the glass has also been identified as one of the steps in the overall corrosion of HLW glasses [DRAN-1988; PETIT-1990c; ABRAJANO-1989]. Water diffusion has been found in natural obsidian weathered for up to tens of thousands of years [e.g., FRIEDMAN-1960, -1978, -1981; MICHELS-1980]. Mazer et al. [MAZER-1991b, -1992a] were able to empirically, yet quantitatively, determine how glass composition, relative humidity, and reaction temperature affect water diffusion in obsidians between 110 and 230°C for times up to 400 days. They observed that the initial water content in rhyolite glasses was an important compositional parameter in these reactions. Both the activation energies and the rates of water diffusion were found to correlate with the logarithm of the initial water content of rhyolite glasses [MAZER-1992a]. The role of water diffusion in a HLW glass corrosion mechanism is discussed more fully in Section 2.1.1.

A naturally altered rhyolite glass 5.2 x 10^3 years old was characterized using scanning electron and optical microscopy [MAGONTHIER-1992]. It was previously determined that this glass had been constantly subjected to low-temperature aqueous corrosion. The alteration products found on the glass surface consisted of a complex sequence of alternating layers of alkali-depleted, Fe-rich aluminosilicate and $Al(OH)_3$. When this same glass was studied under leaching conditions at 120°C for 13 hours, examination of experimentally altered surfaces did not result in the detection of any alteration products. From the results of RNRA analyses, it was postulated that a hydrosilicate had formed on the glass surface that was similar to the alteration layer found on the naturally altered glass. In a comparison of the known range of alteration conditions for natural rhyolite glasses of great age to conditions expected in a repository, Magonthier et al. found that massive deposits, intensive fracturing, subaerial environments, and relatively low-temperature long-term corrosion were common to both systems [MAGONTHIER-1992]. This study concluded that ion exchange was the long-term rate-controlling process for the natural glass studied, based on the assumption that the alternating sequence within the surface layers resulted from simultaneous dealkalization and precipitation.

Rhyolite glasses (obsidians) were considered as a natural analogue for HLW glass because they have relatively long-term chemical stability (up to 6.7 x 10^5 years). Malow and Ewing [MALOW-1980b] determined leach rates for obsidians and waste glasses between 50 and 200°C for up to 3 days. All volcanic glass leach rates were lower than those of the HLW glasses. The authors concluded that volcanic glasses were more stable than the three waste glasses considered.

In general, experimentally determined rhyolite glass leach rates are lower than those for proposed HLW glasses [MALOW-1980b; KARKHANIS-1980]. There is no clear consensus as to the dominant reaction process for rhyolite glasses under leaching conditions. Ion exchange [MAGONTHIER-1992; FRIEDMAN-1984], congruent dissolution (network hydrolysis) [MALOW-1980b], and secondary mineral formation [DICKIN-1981; KARKHANIS-1980; MAZER-1992c] are among the processes reported for these reactions. In one experimental study

[MAZER-1991b, -1992a, -1992c], the reaction of rhyolite glass with water under weathering conditions was found to be dominated by molecular water diffusion. The long-term rate-controlling reaction for rhyolite glass has been described as ion exchange [MAGONTHIER-1992]. If it can be shown that ion exchange plays a similar role in the reaction mechanism for HLW glasses, then rhyolite glasses can play an important role in assessing the long-term durability of waste glasses. Studies on rhyolite, basalt, and tektite glasses are summarized in Table 5-2.

5.3 Tektites

Tektites are generally more silica-rich and alkali-poor than HLW glasses (see Table 5-1). The reaction of tektite glass with water has been found to be strongly dependent on the reaction conditions [MAZER-1992c]. When tektite was reacted in leach tests, the reaction was described as controlled by stoichiometric dissolution and without secondary mineral formation [e.g., BARKATT-1984b; LAMARCHE-1984]. However, in a vapor atmosphere, the reaction was dominated by molecular water diffusion [MAZER-1991b]. A hydrated alteration layer formed on the glass surface that eventually transformed into secondary minerals, including smectite clay. Mazer et al. showed that the relationship between the rate of water diffusion and the intrinsic water content in tektite was consistent with that found for rhyolite glasses [MAZER-1991b] (see Section 5.2). These studies estimated the rate of water diffusion in HLW glasses at 90°C to be 0.01 $\mu m/d^{1/2}$ [MAZER-1992c]. It was assumed that water diffusion into tektite glasses is analogous to that in HLW glasses because of their similar initial water contents [MAZER-1992a].

Studies of tektites under low S/V reaction conditions have found these glasses to be durable materials [BARKATT-1984b; LAMARCHE-1984]. The studies concluded that tektite dissolves stoichiometrically at low corrosion rates compared with other natural glasses.

5.4 Summary

- Natural analogue studies attempt to provide a basis for relating the corrosion of natural glasses of great age to the projected reaction of nuclear waste glasses under repository conditions.

- Basalt glasses, the natural glasses that are compositionally most like nuclear waste glasses, form alteration minerals that are similar to those that form on nuclear waste glasses.

- Rhyolite glasses react somewhat similarly to nuclear waste glasses. The natural and experimental alteration of rhyolite glass is often dominated by the inward diffusion of molecular water, a process also relevant to nuclear waste glass corrosion. Tektite glass reaction results in alteration minerals similar to those found on rhyolite glasses.

- Natural analogue studies can provide confidence that observations in short-term laboratory experiments are relevant to the long-term projections of waste glass behavior by demonstrating that alteration minerals and reaction mechanisms observed in laboratory tests are similar to those observed for natural glasses corroded over very long periods of time. For example, the results for basaltic glasses [YASUHISA-1990] indicate similarities in the observed surface phases and provide evidence for the long-term importance of dissolution controls on the corrosion rate.

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APPENDIX A. WASTE GLASS PRODUCTION AND PROCESS CONTROL

The purpose of this appendix is to provide a general description of the high-level radioactive waste to be vitrified in the U.S.; how it will be vitrified; what is required by the Waste Acceptance Product Specifications; and how the three U.S. sites, SRS, West Valley, and Hanford, will process this waste and control their operations.

A.1 Description of High-Level Radioactive Waste (HLW)

Chemical reprocessing of spent nuclear fuel and irradiated targets reclaims about 99.5% of the uranium and plutonium [WICKS-1989]. A variety of fission products, activation products, trace U/Pu, non-fuel components, and reprocessing chemicals remain after reprocessing. Defense high-level waste is the term used for the waste generated from the U.S. defense programs. Plans have been developed to vitrify 397,000 m^3 of defense high-level waste containing over 1 billion curies of radioactivity [IDB-1991]. This waste is stored as sludge, salt, and supernatant liquid in an alkaline form in large underground carbon steel tanks at the Savannah River Site, SC, and at the Hanford reservation in Hanford, WA. The sludge contains approximately 60% of the radioactivity and essentially all of the actinides and most of the other long-lived species. The remaining 40% of the radioactivity (primarily from cesium) is in the soluble portion of the tank waste [BAXTER-1979]. Another type of waste to be vitrified is the mostly commercial high-level radioactive waste which is present in both mildly alkaline and acidic liquid forms at West Valley, NY, where it was generated as a result of reprocessing of spent commercial fuel rods.

Since these high-level radioactive wastes result from the reprocessing of nuclear fuel, there are general similarities in the waste compositions from the three waste sites selected for borosilicate glass vitrification (Savannah River, West Valley, and Hanford) in the United States. For example, most of the spent fuel and irradiated targets were subjected to Purex processing yielding a high iron content in the waste. Although there are similarities in the wastes, there are also significant differences, particularly in the ranges of waste compositions. These differences arise as a result of the different types of fuel assemblies, the different chemical processing to which the spent fuel was subjected, and the chemical and physical forms in which the waste was stored.

The Savannah River Site currently has 131,700 m^3 of waste from two different processing operations: Purex and HM. This waste, which has a radioactivity of 562 MCi [IDB-1991], is stored in 51 tanks [PED-1988]. The Purex (Px) process was used to extract both plutonium and uranium. The HM process (a modified Px process) was used to recover enriched uranium from uranium-aluminum alloys.

A relatively small amount (~0.3 vol.% of the total U.S. high-level waste) of waste is contained in two tanks at West Valley [IDB-1991]. This waste resulted from recovering uranium and plutonium using two processes: Purex and Thorex. Before the start of the pretreatment of the Purex waste, West Valley stored about 2320 m^3 of high-level waste (2270 m^3 from Purex and 50 m^3 from the Thorex process). The pretreatment of Purex supernatant has resulted in about 45 m^3 of zeolite IE-96 loaded with radioactive cesium and a volume reduction to about 1140 m^3 of an alkaline waste. The total radioactivity of this HLW is about 27 MCi [IDB-1991].

The Hanford site has 253,600 m^3 of waste (393 MCi of activity) which is stored in 177 tanks (28 double shell and 149 single shell) [IDB-1991]. This waste resulted from four different chemical processing operations [IDB-1991, HWFA-1990] including bismuth phosphate, redox, and Purex processes for the recovery of plutonium and the tributyl phosphate process for recovery of uranium. Of the three U.S. liquid waste sites, the ranges of composition are widest at Hanford because of the number of different reprocessing methods which were employed [HWFA-1990].

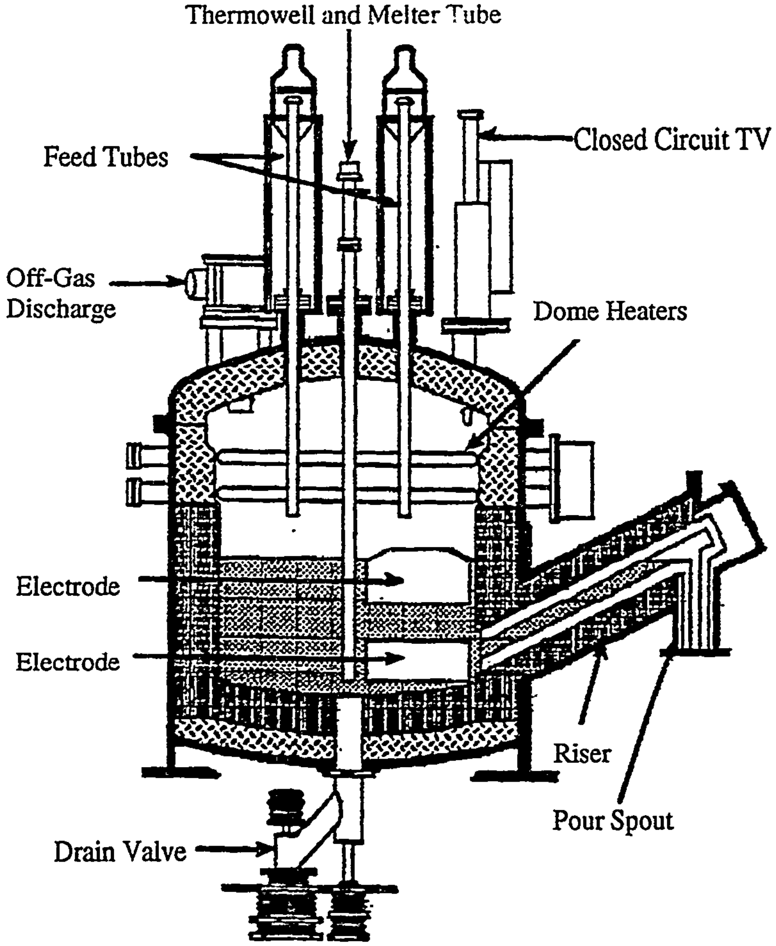
With most of the high-level radioactive wastes in the United States being stored in potentially dispersible, liquid form in carbon steel or stainless steel tanks [IDB-1991], efforts to change this waste into a more stable solid form, which will be suitable for storage, transportation, and eventual disposal, are being pursued. The high-level waste will be subjected to a number of processing steps to reduce its volume and prepare it for conversion into borosilicate glass waste forms.

A.2 Vitrification of Waste

Vitrification of high-level radioactive waste in the U.S. will be accomplished in slurry-fed, joule-heated, ceramic-lined melters. Figure A-1 illustrates some of the characteristics of the DWPF melter. It will be fed and poured continuously. A full melter will hold enough glass to fill 4-5 canisters or about 7500 kg of glass. The average residence time of the molten glass in the melter will be 65 hours. The glass batch will be melted by Joule heating using two pairs of flat, parallel, inconel electrodes immersed in the melt. The glass will be poured by a vacuum process. An advantage of a ceramic-lined melter is that ceramic refractories are more temperature and corrosion resistant than typical metal liners thus yielding higher melter life expectancy. Development of the slurry feeding concept was an important development for the vitrification of nuclear waste. Slurry feeding significantly reduces capital costs and greatly simplifies the operation [WICKS-1985] by eliminating the need to either dry or calcine the slurry prior to vitrification. Slurry feeding eliminates the capital cost of calcining and yields a more homogeneous feed.

Feed slurry is introduced through the top of the melter. As the water evaporates from the feed, it is removed via the off-gas system. The solids in the feed slurry form a crust or cold cap on the surface of the melt pool. This cold cap reduces the volatility of the melt. Immersed electrodes supply electric power directly to the melt. The nominal glass temperature beneath the cold cap is 1150°C, but varies throughout the melter. The cold cap melts from the bottom and forms the borosilicate waste glass. Convection currents which are established in the molten glass as a result of the localized electrical heating and accompanying density differences assist in homogenizing the glass. Glass is removed from near the bottom of the melter through a riser and pour spout or via a drain valve. Molten glass is poured into stainless steel canisters and allowed to cool. The canisters are then decontaminated by a frit blasting operation at Savannah River Site and Hanford. A temporary plug will be employed during the frit blasting operation to prevent contamination from entering the canisters. The canisters will be permanently sealed with a canister closure plug by resistance welding (at SRS) and arc welding at West Valley. West Valley canisters will be decontaminated after welding via a chemical decontamination process.

The U.S. process differs in some significant ways from the French AVM melting process which employs an Inconel 600/601 vessel with induction heating [HWFA-1990, TWT-1991]. The U.S. and the French AVH melters operate at similar temperatures. For example, the control temperature for the DWPF melter is 1150°C as compared to a peak wall temperature of 1170°C for the AVH melter. The glass centerline temperature in the AVH melter is 1080°C. Since the U.S. melters have electrodes immersed in the molten glass rather than a heated outside wall, temperature



Melter Characteristics	
Weight of assembly filled with glass	73,000 kg
Total melter volume	5.5 m^3
Average glass volume	2.5 m^3
Glass height along sidewall	0.86 m
Glass height along centerline	0.95 m
Melter diameter	1.8 m
Pour spout inside diameter	5 cm
Riser angle	25° 30'

Fig. A-1. DWPF Melter System

gradients should be somewhat lower and therefore overall temperatures will be similar between the two types of melters. French waste in liquid nitrate form is calcined prior to being fed directly into the melter. The high alkali content of most of the U.S. waste, which promotes clinker formation, makes calcination an impractical option because of clogging problems in the calciner. Crushed glass is added simultaneously, although separately, until the melter is full. After the waste and glass have reacted for about 8 hours, the melter is drained through the bottom. The AVM melter is emptied during each pouring into a canister. A total of three pourings are required to fill each canister.

A.3 Waste Acceptance Product Specifications

From a production perspective, the main determinant of a satisfactory borosilicate waste glass and, in turn, a satisfactory canistered waste form is satisfying the requirements of the DOE Office of Environmental Restoration and Waste Management's (EM) Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms [WAPS-1993]. These specifications define the criteria that the waste glass products must satisfy before they will be accepted by the U.S. DOE Office of Civilian Radioactive Waste Management (OCRWM) for disposal. They are divided into five sections, dealing with the waste form(borosilicate glass), the canister, the canistered waste form, quality assurance, and documentation. The underlying rationale for most of the specifications of the EM-WAPS can be traced to the DOE Office of Civilian Radioactive Waste Management's Waste Acceptance Systems Requirements Document (WA-SRD-1993).

The waste form must be borosilicate waste glass [WAPS-1993]. The chemical composition, crystalline phase projections, radionuclide inventory, a Product Consistency Test result or projection, and other characteristics must be reported for the glass. The canister must be fabricated from austenitic stainless steel to specific dimensions and be identifiable. The canistered waste form must be sealed closed, be free of foreign materials, meet heat generation and dose limits, be capable of surviving a specific drop, and meet other requirements.

A.4 Effects of Composition of Melter Feed on Vitrification

Just as the expression "high-level waste" does not refer to one waste composition, the expression "borosilicate glass" does not refer to one glass composition, but instead to the family of compositions whose primary glass-forming ingredients are boron and silicon. Borosilicate waste glass is a vitreous material which incorporates the constituents of the high-level waste directly into its structure. It can accommodate many different elements and wide variations in waste composition [WICKS-1985]. However, the composition of the melter feed has to be controlled to achieve a satisfactory product and to meet processing constraints.

The chemical composition of the melter feed is the primary determinant of the chemical durability of the waste glass product and many of the important melt processing properties (e.g., viscosity and liquidus temperature). Thus, chemical composition of the melter feed is the most important variable to be controlled. Because an incorrectly formulated glass cannot be remediated once it has been poured into a canister, the feed composition must be correct. Provisions have been developed for disposition of nonconforming canisters. Depending on the type of nonconformance involved, the disposition may involve sending the canister involved to the repository or retaining it indefinitely at the producing site. The selection of either the frit composition or the blend of glass-forming chemicals for a given waste composition is made based on the desired waste loading, the composition of the high-level radioactive waste, and processing considerations.

In contrast to crystalline materials, which have distinct, sharp melting temperatures, glass batches melt (react) over a range of temperatures which depends on the glass composition. Borosilicate glasses comprise a smaller portion of this melting temperature range but still span the range from moderate to relatively high melting temperatures. Low melting temperatures (1050 to 1150°C) facilitate operation within the realm of Inconel electrode temperature limits and allow remotely operated processing, efficient offgas treatment, and reasonable equipment lifetimes. Obtaining the best compromise of product properties and processing characteristics is one of the challenges involved in waste glass production and is a major function for the process control system.

The compositions of nuclear waste glasses vary based on the particular balance of physical, chemical, and thermal properties which is desired, the types of equipment being used for processing, and the types of waste being processed. The viscosity of the glass melt must fall within a carefully defined range to assure that the glass will melt properly, will be properly homogenized via viscous flow within the melter, and will pour from the melter. If the viscosity is too low, excessive attack on the refractories in the melter will result. The temperature at which crystals begin to form in the glass if the temperature is maintained below a minimum temperature, termed the glass liquidus temperature, is also determined by the glass composition. Components that tend to make the glass more durable also tend to raise its viscosity and its liquidus temperature. Higher viscosities make processing more difficult while higher liquidus temperatures can result in increased volatilization. The goal of tailoring the glass composition is to obtain the optimum balance of all the important glass properties.

High-level radioactive waste is added at selected waste loadings to borosilicate glass frit or to components which when melted together will form the desired borosilicate glass matrix. The primary ingredients of the borosilicate glass frit are silica (SiO_2), boron oxide (B_2O_3), and alkali metal oxides (Na_2O, K_2O, and Li_2O). Other ingredients are added to obtain a balance of glass properties [RAMSEY-1989]. Since high-level radioactive waste consists primarily of alumina (Al_2O_3), iron oxide (Fe_2O_3), and manganese dioxide (MnO_2), addition of high-level radioactive waste to borosilicate glass frit enhances the short-term durability of the product. The normalized release of specific components may decrease by a factor of 5 over that of the borosilicate matrix glass without radioactive waste [CLARK-1982, WICKS-1985]. When waste loadings of 40% or more are reached, the glass structure is so perturbed that rearrangement of atoms into more stable crystalline structures with accompanying changes to the chemical composition of the remaining glassy phase is favored [RANKIN-1983, WICKS-1985]. For this reason lower limits on waste loading are employed. Effects of waste constituents on important glass processing and product properties are shown in Table A-1 [PLODINEC-1982].

A.5 SRS Processing and Process Control

Projections of the chemical composition of the existing waste inventory at the Savannah River Site are principally based on chemical analyses of individual samples of the waste taken directly from the waste tanks. Several general types of waste currently reside in the waste tanks, including HM/Px/hh[1] waste, HM/Px/lh waste, Px/hh waste, Px/lh waste, and some others. Three feed streams will be prepared and combined to form the final feed to the Defense Waste Processing Facility (DWPF) melter. These three feed streams are a precipitate feed called precipitate hydrolysis aqueous (PHA), a sludge feed, and glass frit. A flow chart of the DWPF process is shown in Fig. A-2.

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[1] HM - high metal (aluminum), Px - Purex, hh - high heat, lh - low heat.

Table A-1. Effects of Frit and Waste Components on Glass Process and Product Properties

Frit Component	Processing Effects	Product Effects
SiO_2 or Al_2O_3	Increases viscosity. Reduces waste solubility.	Increases durability.
B_2O_3	Reduces viscosity. Increases waste solubility.	Increases durability at low levels. Reduces durability at high levels.
Na_2O or K_2O	Reduces viscosity.	Reduces durability.
Li_2O	Similar effect as with Na_2O but more effect for same % addition. Increases tendency to devitrify.	Reduces durability, but less effect than for same % addition of Na_2O
CaO	Increases viscosity and waste solubility for low % additions. High levels decrease viscosity and waste solubility.	Low levels increase, high levels decrease durability.
MgO	Same effect as with CaO. Decreases tendency to devitrify.	Same effects as with CaO.
TiO_2	Reduces viscosity slightly. Low levels increase, high levels decrease waste solubility.	Increases durability. Increases tendency of waste to crystallize.
ZrO_2	Reduces waste solubility.	Increases durability.
Waste Component		
Al_2O_3	Increases viscosity and tendency to crystallize.	Increases durability.
FeO	Lowers viscosity.	Decreases durability. Increases tendency to crystallize.
Fe_2O_3	Hard to dissolve in glass.	Increases durability.
U_3O_8	Reduces tendency to crystallize.	Minimal.
MnO_2	Hard to dissolve in glass.	Increases durability.

Note: Some components could possibly be in the waste rather than in the frit or visa versa. The effect of the particular component would still be the same as stated.

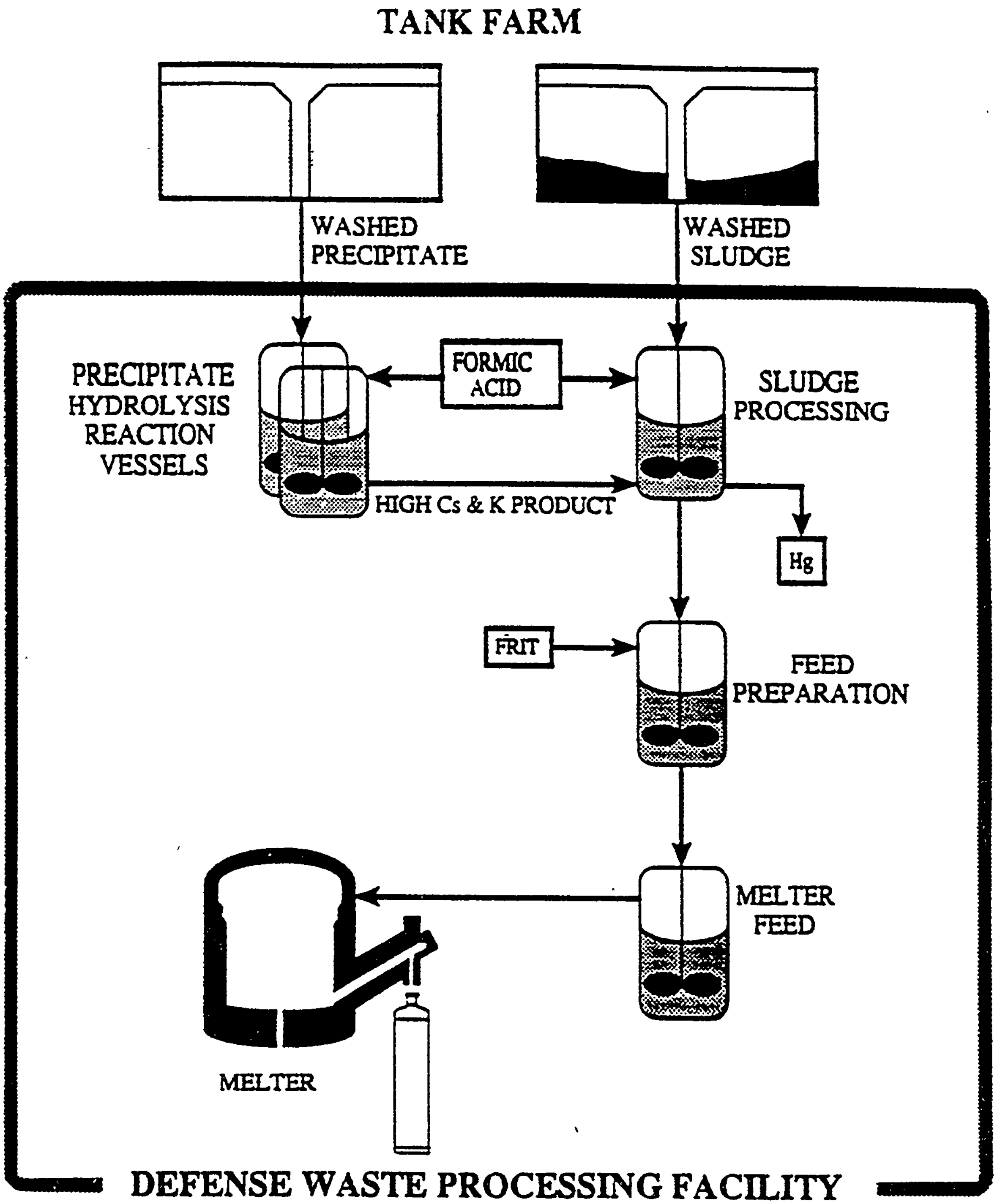


Fig. A-2. Immobilization of SRS High-Level Radioactive Waste

A.5.1 SRS Waste Processing

A precipitate feed product will consist of radioactive cesium, nonradioactive potassium tetraphenylborate, and trace amounts of strontium-90 and plutonium sorbed onto sodium titanate. This product, termed PHA, will be formed by adding sodium tetraphenylborate and sodium titanate to the supernatant liquid in the tank farm in order to separate out the radioactive constituents. This treated supernatant liquid will be subsequently filtered, producing the PHA. After the PHA waste arrives at DWPF, formic acid, hydroxylamine nitrate (HAN), and a copper catalyst will be added to neutralize the waste and to remove the organic portion. These additions will also cause any mercury dissolved in the precipitate slurry to precipitate out of solution, whereupon it will be removed.

Preparation of the sludge feed will begin with washing of the sludge in the storage tanks at the tank farm. Further processing will be done after the washed sludge has been transferred from the storage tanks to DWPF. Formic acid, or possibly nitric acid, will be added to lower the pH from ~12 to ~7. The effect of chemical reducing agents (i.e., formic acid) on the sludge will cause any mercury present to be reduced and subsequently to precipitate. Thereafter this washed/neutralized sludge is ready for vitrification.

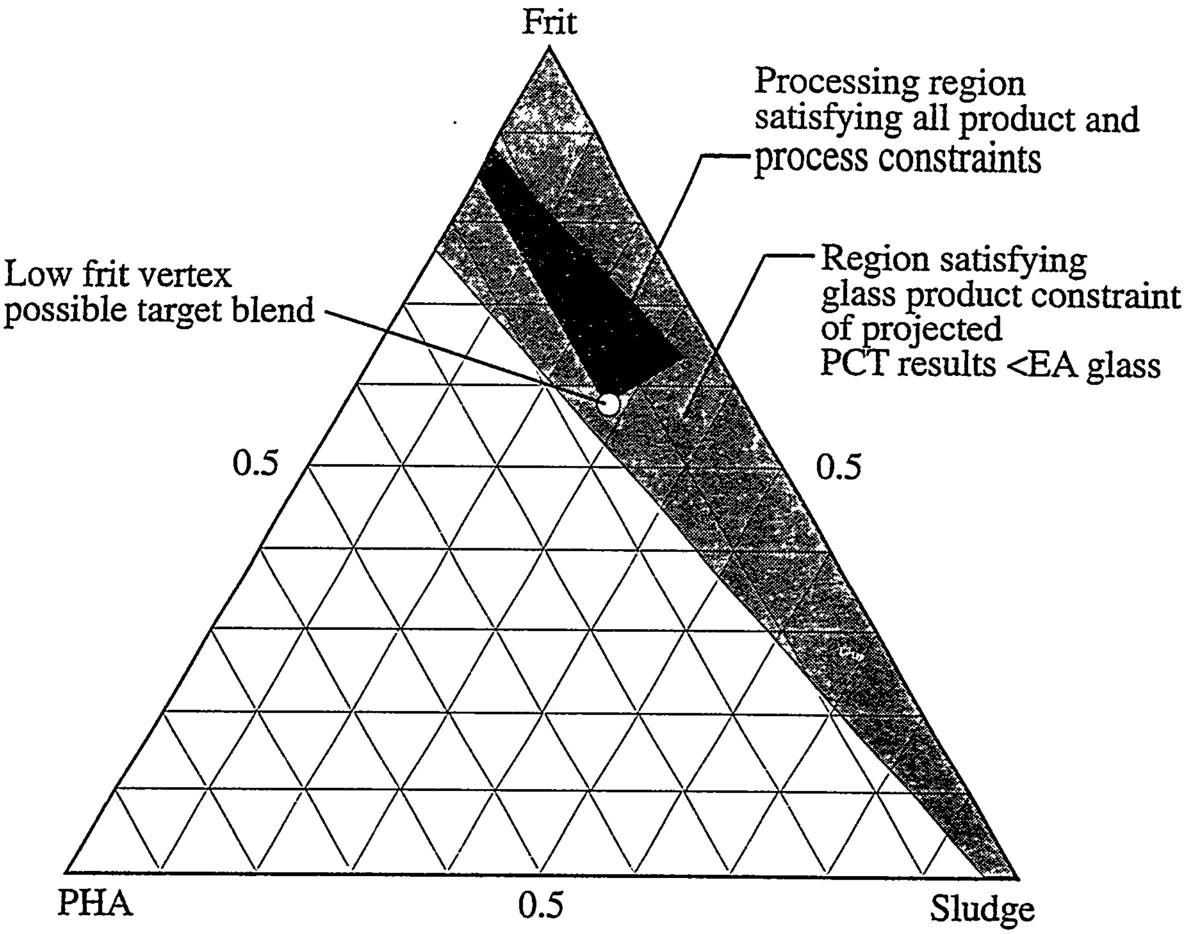
Within the vitrification building, about 90% of the organic content of the tetraphenylborate salt is removed by hydrolysis with formic acid. This is necessary to avoid overly reducing conditions in the melter and the off-gas system. The aqueous product, which contains the cesium, boron, and the insoluble titanate with sorbed Sr and Pu, is then mixed with the washed sludge.

The DWPF will mix sludge, precipitate, and frit in a 28:8:64 ratio, on an oxide weight percentage basis to form the final borosilicate waste glass product. This nominal feed ratio yields a waste loading of about 36 wt.% for DWPF. This nominal feed composition is only approximate since acceptable feed compositions will span a range of compositions. All compositional adjustments to yield the final desired waste glass composition, which is the primary determinant of a satisfactory product, are made during the sludge, precipitate, and frit blending process.

A.5.2 SRS Process Control

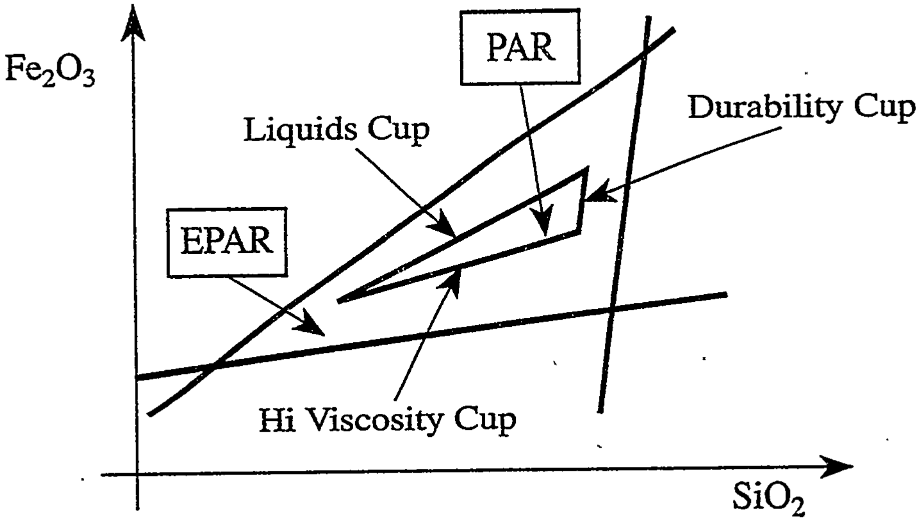
A blend target is set initially based on the assayed compositions of the feed components (sludge, PHA, and frit). Determining how much of each component is required in the final blend is the goal of target blending (Fig. A-3). Blends can be made from binary combinations of frit and sludge or frit and PHA. A ternary blend of frit, sludge, and PHA, which is the goal, narrows the field of acceptability further. The shaded triangular region shown in Fig. A-3 shows a conceptual region of compositions that should have acceptable free energies of hydration. (Note: The free energy of hydration is correlated with the short-term leachability as discussed in Section 2.2.) Adding the limits for liquidus temperature and viscosity reduces the area within the shaded region much more as shown by the dark triangle within the shaded triangle. The low frit vertex shown in this figure is not itself a target composition but is shown to indicate the lowest frit composition (~58 wt.%) which could yield acceptable properties. Still lower frit compositions are possible, but not acceptable.

Figure A-4 shows a conceptual blending diagram for two waste glass components, Fe_2O_3 and SiO_2, plotted in two dimensions (the blending of all components (a total of n) would have to be plotted in n-1 dimensional space since all components are considered simultaneously). Continuing the simplified discussion of two components, blending of these two would be done such that the glass made from the final blend would have a durability, liquidus temperature, and viscosity falling within



PHA – Precipitate Hydrolysis Aqueous
EA glass – Environmental Assessment glass
Low Frit Vertex – Highest Waste Loading

Fig. A-3. Nominal PHA/Frit/Sludge Target Blending Diagram (wt. fractions) (adapted from [SRWCP-1992]).



EPAR – Expected Property Acceptable Region
CUP – Composition Uncertainty Plane
A and B are any two arbitrary components of the glass

Fig. A-4. A Conceptual Property Acceptable Region (PAR) for Two Arbitrary Components of the Glass (adapted from [POSTLES-1991]).

the desired limits (e.g. within the EPAR region of Fig. A-4). Then the acceptable compositional region would be contracted further based on the errors and uncertainties in the measurements (Fig. A-4).

Blending requires assessing many candidate composition points and then selecting a unique narrow range therefrom. Concentrations of individual elements in the blend cannot be set totally at will since a series of elemental components makes up each feed stream and thus each elemental component cannot be adjusted individually and impurities cannot be removed. Thus, not all conceptually possible compositions can be made from a blend of a particular feedstock inventory. An optimum blend is one that maximizes the amount of waste (sludge + precipitate slurry) while maintaining waste glass durability and other product and process variables within acceptable limits. A feed slurry batch is monitored for property acceptability by checking whether its composition lies within a property acceptable region (Fig. A-4). After the feed composition has been selected and prepared, samples taken from the process vessel are assayed. If the slurry batch is deemed to be capable of producing acceptable waste glass after confirmation analysis, it is cleared for transfer to the melter. If it is unacceptable, trim chemicals (sodium hydroxide, potassium hydroxide, or boron oxide) or additional frit can be added to move it into an acceptable region. The mixed feed will not be transferred until its composition is suitable for producing acceptable glass (Fig. A-5).

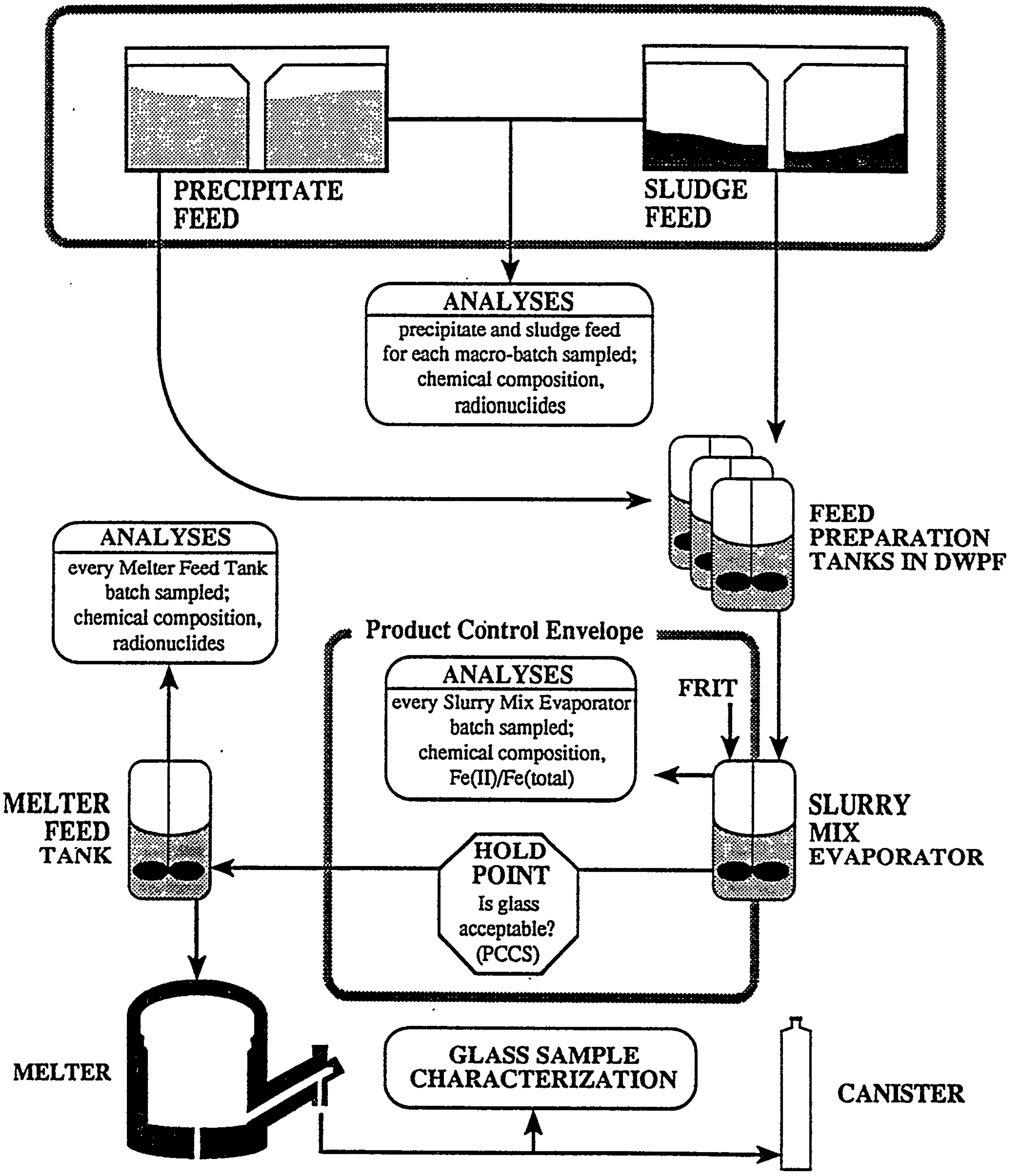


Fig. A-5. DWPF Product Control

The variability of each component, the extensive ranges of compositions to be considered, and the complex regression analysis required for numerous correlations dictate computer computation for glass formulation and control. Toward this end, the Product Composition Control System (PCCS) [SRWQR-1992] was developed at SRS to control the feed slurry composition. The PCCS consists of statistical process control algorithms and composition/property correlations. Composition/property correlations are used to determine acceptability of the feed slurry by transforming the concentrations and variabilities of individual slurry elements into predicted final glass properties as shown schematically in Fig. A-4 for two components, Fe_2O_3 and SiO_2. Statistical process control algorithms are then used to determine the level of confidence in the accuracy of the final glass composition.

The basis for process control of the melter feed composition is the correlations between the chemical composition of the feed and the physical properties of the resultant glass [POSTLES-1991; JANTZEN-1991, -1992]. The free energy of hydration model [JANTZEN-1989, -1992] will be used to predict the short-term durability [Product Consistency Test (PCT)] of the glass from its composition [PLODINEC-1992]. A glass is assumed to be an ideal mixture of silicate and oxide components (i.e., no free energy of mixing between components). The total free energy of hydration of a glass (see Section 2.2) is assumed to be the sum of the free energies of hydration of each of the glass components weighted by its concentration in the glass. PCT testing of the EA glass has produced a free energy of hydration of about -10 kcal/mole. Thus for acceptability PCT testing of a waste form would have to demonstrate a free energy of hydration statistically better (more positive) than that of the EA glass [WAPS-1993].

Prior to transfer to the melter, the feed will be sampled and analyzed. The analyzed composition, after accounting for experimental uncertainty, must fall within the bounds for producing acceptable product. Only after the feed has been deemed, using the PCCS, to be capable of producing acceptable glass (i.e., glass that satisfies preestablished durability, viscosity, and liquidus temperature constraints), (see Figs. A-2 and A-3) will it be fed to the melter. The DWPF canisters will be filled in a continuous operation; as molten glass is removed from the melter, additional feed is supplied. Table A-2 shows the acceptance ranges for glass viscosity, liquidus temperature and free energy of hydration for DWPF glass. The corresponding acceptable ranges for DWPF waste glass components are shown in Table A-3.

A.6 West Valley Processing and Process Control

West Valley has four storage tanks. One contains PUREX waste, one contains THOREX waste, one contains cesium-loaded zeolite, and the fourth is a spare. A number of chemical processing steps will be taken to prepare the HLW for vitrification and to minimize the final volume of waste glass. A single glass composition will be produced from the combined waste.

A.6.1 West Valley Waste Processing

Zeolite IE-96 ion exchange columns are used to remove cesium from the PUREX supernatant. After the ion exchange process has been completed, the sludge will be washed to remove soluble sulfates and interstitial supernatant. The THOREX waste will be transferred to and mixed with PUREX sludge. Then the cesium-loaded zeolite will be combined with the THOREX and PUREX sludges to produce a single mixture. Prior to analysis, this slurry will be transferred to a concentrator feed makeup tank, blended, and evaporated to concentrate the slurry. Analysis of this concentrate will be used to determine the amount of glass-forming chemicals which must be added to obtain the desired final waste glass feed composition shown in Table A-4 [WVWCP-1991].

Table A-2. Glass Property Ranges for DWPF Glass

Property	Units	Criteria
Viscosity	Poise	$20 < \text{visc.} < 100$
Liquidus Temperature	°C	< 1050
Durability	kcal/mole	$\Sigma\Delta G_{hyd} < -7.0$

Table A-3. Component Ranges for DWPF Waste Glasses

	Range (wt. %)	
Component	Minimum	Maximum
SiO_2	44.6	54.4
Al_2O_3	2.9	7.1
B_2O_3	6.9	10.2
CaO	0.8	1.2
MgO	1.3	1.5
Na_2O	8.2	12.1
K_2O	2.1	4.6
Li_2O	3.1	4.6
Fe_2O_3	7.4	12.7
MnO	1.6	3.1
TiO_2	0.6	1.0
U_3O_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

[a] Isotopes of Tc, Se, Te, Rb, Mo.

[b] Isotopes of Ag, Cd, Cr, Pd, Ti, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, Cm.

This waste slurry mixture will be blended, reanalyzed to verify attainment of the target composition, and then transferred to the melter feed tank. A final blend on a weight basis of 19% washed Purex sludge, 5% Thorex waste, 17% Cs-loaded zeolite, and 59% cold chemicals will be used to produce a single glass composition shown in Table A-4. The melter feed tank enables a transition from the batch slurry preparation cycle to a continuous melting operation to be made. The slurry from the melter feed tank will be pumped directly to the melter.

A.6.2 West Valley Process Control

The basis for control of the single West Valley glass target composition containing all of the HLW constituents is shown in Table A-5 [WVWCP-1991]. The level of each component listed is adjusted to bring each into the appropriate range. The basis for verifying attainment of the desired slurry composition is to show a 95% confidence that each oxide present in the glass at greater than 0.5% falls within the bounds given in Table A-5. One slurry batch is expected to produce about three canisters. After the glass-forming chemicals have been added and mixed, another chemical analysis will be performed to verify that the waste/glass-former slurry composition is correct. Only after the slurry batch has been determined to be acceptable will it be fed to the melter.

A redox target of 0.02-0.5 Fe^{2+}/Fe^{3+} has been established. A reducing agent, probably sugar, will be added to the batch to obtain the desired redox state.

In the melter the remaining water will be evaporated from the slurry and the solids from the feed will begin to react. The partially reacted waste and glass forming additives melt into the glass pool. Molten glass is intermittently poured into stainless steel canisters. Approximately 10-15 pour cycles will be required to fill each canister. The filled canisters will be transferred to the capping station. The canister lid will be welded to the top flange of the canister using a tungsten/inert gas process. The canister will then be transferred to the decontamination system where the external surfaces of the canister will be cleaned by chemical etching using a nitric acid/cerium solution. Following decontamination, the canisters will be transported to interim storage.

A.7 Hanford Waste Processing

The Hanford Site has nuclear wastes stored in both single shell and double shell tanks. The current baseline vitrification program calls for pretreatment and disposal of the high level waste in 10 of the 28 double shell tanks [IER-1991, TWT-1991, HWPWF-1991]. Four waste types to be vitrified include Neutralized Current Acid Waste (NCAW), Neutralized Cladding Removal Waste (NCRW), Plutonium Finishing Plant waste (PFP), and Complex Concentrate waste (CC) [HWPWF-1991]. Approximately 105 MCi of radioactivity are contained in these wastes which are comprised of sludge, precipitated salts, and supernate which contains radioactive cesium.

A redefinition of the current baseline program at Hanford is underway which may substantially increase the scope of the current vitrification program to include the single shell tank wastes and encapsulated cesium and strontium sources previously separated from the process wastes. For this reason, it is premature to outline the waste processing and process control for the Hanford site.

Table A-4. Nominal Oxide Content of the West Valley 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_2O_3	0	1.2	0	21.8	12.9
Fe_2O_3	57.6	12.9	2.4	0	12.1
Na_2O	7.6	1.1	13.9	6.9	8.0
K_2O	0	0.6	23.5	1.5	5.0
Li_2O	0	0	0	6.3	3.7
Al_2O_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_2O_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

[a] Includes radioactive cesium.

[b] Constitutes other components each present at less than 0.5 wt.%.

Table A-5. West Valley Potential Target Glass Processing Region

Component	Lower Bound (wt %)	Upper Bound (wt %)
SiO_2	38.8	43.2
B_2O_3	11.0	14.8
$K_2O + Li_2O + Na_2O$	14.7	18.8
Fe_2O_3	10.2	13.8
Al_2O_3	5.4	6.6
BaO + CaO + MgO	1.2	1.6
MnO	0.7	0.9
P_2O_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

[a] Other includes CeO_2, Cr_2O_3, Cs_2O, CuO, La_2O_3, MoO_3, Nd_2O_3, NiO, PdO, Pr_6O_{11}, Rh_2O_3, RuO_2, SnO_2, TeO_2, Y_2O_3, and ZnO.

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APPENDIX B. SUMMARY BY COUNTRY OF INTERNATIONAL EXPERIENCE

This Appendix is a survey of worldwide research and development efforts on nuclear waste glass and production technology. Summaries of the R&D activities of each country active in developing vitrification technology are given in the Appendix. The reader is referred to the proceedings of the international symposium *Scientific Basis for Nuclear Waste Management* sponsored by the Materials Research Society for a comprehensive resource of information on waste form materials research and technology development. In preparing this chapter, we have drawn heavily on a recent report "National Briefing Summaries: Nuclear Fuel Cycle Research and Development" [SCHNEIDER-1991], issued by the International Program Support Office (IPSO) at the Pacific Northwest Laboratory (PNL), for a compilation of information concerning the radioactive waste management programs of 23 nations and three international agencies that have made public their activities in this field. Additional information was obtained from Radioactive Waste Forms for the Future edited by Lutze and Ewing [LUTZE-1988] to provide a worldwide survey of available literature through the mid-1980's on alternative high-level waste forms, including borosilicate glasses.

B.1 Argentina

Nuclear Power Capacity (2020)	14 GWe
Reactor Mix (planned)	6 PHWR
Reprocessing Plant	Ezeiza, Argentina
Expected Glass Production (2030)	1500 m^3

The Comision Nacional de Energia Atomica (CNEA) is planning to build facilities for borosilicate glass production with a 160 kg/d capacity using the French AVM process. The plant is to be operational by the late 1990s. A reprocessing pilot plant at the Ezeiza Atomic Centre, near Buenos Aires, may be expanded into the commercial facility for glass production

Argentina's strategy for high-level waste disposal is to screen candidate sites leading to the selection of one site for detailed characterization. The reference disposal concept is for a 1 km^2 repository area located in granite at a depth of approximately 500 m. The repository capacity is expected to be 3000 canisters of approximately 0.6 m in diameter and 1.6 m long. A packing of bentonite/quartz sand is also planned. The maximum thermal power of each package is expected to be 500W with a maximum thermal loading of 5 W/m^2. The maximum emplacement temperature is 60°C.

B.2 Belgium

Nuclear Power Capacity (2000)	5.5 GWe
Reactor Mix	7 PWR
Reprocessing Plant Location	La Hague, France
Expected Glass Production (2030)	850 m^3

In Belgium, the utilities decide whether to reprocess and recycle spent fuel. Currently, spent fuel is being reprocessed in France and the vitrified HLW being returned to Belgium for disposal. Between 1966 and 1974, the Eurochemic reprocessing plant was operated at the Mol-Dessel site as a joint undertaking of 13 OECD/NEA member countries. The plant processed 181.5 MT of natural and slightly enriched uranium fuel. Approximately 60 m^3 of "low enrichment waste concentrate" (LEWC) from this campaign have been vitrified at the Pamela facility to produce 64 MT or 23 m^3 of glass.

The Pamela facility was built between 1981 and 1984 as a joint construction project with the Federal Republic of Germany to demonstrate the liquid-fed ceramic melter process. The Pamela facility is now being used to vitrify 765 m^3 of HLW from reprocessing of high-enrichment spent fuel.

Two reference (nonradioactive) glasses for the Pamela vitrification system have been studied extensively: SM58LW11 and SAN6025. The compositions are given in Table B-1. Both laboratory and underground testing of these glasses is being conducted by the Centre d'Etudes de l'Energie Nucleaire/Studiecentrum voor Kernenerqie (CEN/SCK).

B.3 Canada

Nuclear Power Capacity (2000)	13.9 GWe
Reactor Mix	18 PHWR (CANDU)
Reprocessing Plant Location	
Expected Glass Production (2030)	None (spent fuel)

Canada's nuclear energy policy is to maintain an independent national nuclear power program using CANDU (CANada Deuterium Uranium) pressurized heavy water reactors (PHWR's) and to export CANDU nuclear reactor and fuel cycle services. Presently, Canada's nuclear fuel cycle policy is to not reprocess spent fuel. Estimates are that fuel reprocessing will not be economic with the once-through CANDU fuel cycle until there is a three-fold increase in uranium prices, which is not likely to occur for at least several decades [DORMUTH-1989a]. While no decision on future reprocessing has been made, geological disposal technology is being developed for both spent fuel and vitrified reprocessing wastes.

Table B-1. Composition of Precursor Glasses (wt%)

Oxide	SM58LW11	SAN6025
Al_2O_3	1.2	18.1
B_2O_3	12.3	17.0
CaO	3.8	3.5
Fe_2O_3	1.2	0.3
Li_2O	3.7	5.0
MgO	2.0	-
Na_2O	8.3	10.7
SiO_2	56.9	43.4
TiO_2	4.4	-
Others	6.2	2.0

The Atomic Energy Control Bureau (AECB) regulates all stages of the nuclear fuel cycle. The Atomic Energy of Canada Limited (AECL) is the federal agency responsible for reactor design, isotope production, marketing, research and development. AECL is responsible for research on immobilization and disposal of spent fuel and operates facilities for processing and storage of LLW and ILW [TORGERSON-1990b]. The AECL/Whiteshell Nuclear Research Establishment (WNRE) directs and coordinates the R&D program on immobilization and safe disposal of nuclear fuel waste. The AECL/Chalk River Nuclear Laboratory (CRNL) has facilities for HLW solidification using in-can melting. The Ministry of Energy, Mines, and Resources (EMR) is the federal government ministry to which AECB and AECL report.

Glass R&D

A nonradioactive pilot plant (WIPE) at WNRE for developing a high-level liquid waste (HLLW) conditioning process for a thorium fuel cycle started operations in 1983 at a glass production rate of 10 kg/hr using a rotospray calciner and joule-heated ceramic melter. From 1980 to 1985, a radioactive reprocessing pilot plant was operated at 0.3 kg/d using a Thorex process in mixer-settlers to provide HLW for waste treatment studies. The Underground Research Laboratory (URL) at Whiteshell (20 km from WNRE) for spent fuel/HLW disposal studies in deep granite formations started underground operations in 1986. It will use licensed radioactive sources and tracers, but no radioactive wastes will be emplaced [RUMMERY-1984, NEA-1986, AECL-1989]. In 1984, the Hydrostatic Test Facility (HTF) and Immobilized Fuel Test Facility (IFTF) were started to test the performance of waste package materials.

Past development of the vitrification process includes hot-cell and engineering-scale tests, design of an industrial-scale facility, evaluation of glass and mineral waste forms, evaluation of waste forms, buffer materials, container materials and host rock under repository conditions (at WNRE), and vitrification using in-can melting at CRNL [WIKJORD-1984; SRIDHAR-1984, -1985]. As of 1988, these programs were completed.

Several concepts for immobilizing reprocessing wastes from fuel recycle have been studied, including borosilicate glasses, sodium alumino-silicate glasses and glass-ceramics. Sodium aluminosilicate glasses have been shown to be superior to borosilicate glasses for calcined reprocessing wastes [ROSSINGER-1988]. Leach rates are low in saline groundwaters characteristic of the Canadian Precambrian Shield. Glass ceramics, based on the natural mineral sphene, give further improvements in leach resistance. Fuel-container research has been focused on titanium alloys and copper, which are particularly resistant to the chloride-rich groundwaters found deep in the Canadian Shield [TORGERSON-1990a, -1990b]. Geochemistry studies of groundwater-rock and waste-rock interactions have included thermodynamics; fission product and actinide chemistry; sorption effects, radionuclide transport in buffer materials and natural fractures, interactions of groundwater with minerals, and colloid phenomena [VANDERGRAAF-1984, -1985; VIKIS-1985; NEA-1986]. Natural analog studies have confirmed the stability of uranium oxide in groundwater at the Cigar Lake uranium deposit where grains of UO_2 with local concentrations up to 60% have remained stable since the ore body was formed about 1.3 billion years ago [DORMUTH-1989b].

A team of Canadian and Japanese scientists has begun a study of 25 vitrified glass blocks buried 30 years ago near Chalk River. The nepheline-syenite glass blocks contain a total of about 5.5×10^{11} Bq (15 Ci) of mixed fission products. The leaching rate (primarily ^{90}Sr) will be measured.

The chemical reactions among radionuclides, groundwater, and solids within the underground flow system will be measured. The experiment will continue through 1992. The existing stack of blocks in five vertical columns will be left in place for future analysis.

B.4 China

Nuclear Power Capacity (2000)	4 GWe
Reactor Mix	5 PWR
Reprocessing Plant Location	Quinshai Province, Gobi Desert
Expected Glass Production (2030)	160 m^3

Two 900-MWe foreign-built PWRs are under construction at Guangdong (Daya Bay) and are scheduled to start up about 1993; two indigenous 600-MWe PWRs are under construction at Qinshan and are scheduled to start up in 1995-1996. This type of 600-MWe unit is expected to be the mainstay of the future China nuclear industry. Other electrical generating units are under consideration, including high-temperature gas-cooled reactors (HTGR); R&D is also under way for future breeders and fusion reactors [PENG-1988; EIA-1989].

In China, spent fuel will be reprocessed to conserve resources and HLW will be vitrified and placed in engineered storage for 30-50 years before final disposal into a geological formation [LUO-1987; NEI-12/87; YANG-1987]. Reprocessing in China uses the PUREX solvent extraction process, using mixer-settlers. Research on various types of pulse columns is in progress [JIANG-1987; DE-XI-1988]. R&D on reprocessing started in the late 1950s for defense purposes. A trial reprocessing workshop was built for military purposes in 1968, and a military reprocessing plant was set up in 1970 in northwestern China [NF-10/3/87]. A 100-kg/d reprocessing pilot plant in the Gobi Desert in the Quinshai Province in north-central China for commercial fuel is scheduled to begin service in 1996 [NEI-2/89]. The plant is to be designed for recovery of a few thousand kg/yr of noble metals for China's petrochemical industry. A larger-scale reprocessing plant is planned to be under construction by about 2000-2010 at the same 20,000-km^2 site in the Gobi Desert as the pilot-scale reprocessing plant. The plant will also recover noble metals, neptunium, americium, and curium from the HLW stream and will include a solidification plant and a permanent burial site for solid radioactive waste [NWN-5/4/89].

China expects by the year 2000 to have accumulated over 1600 MT of spent fuel for 10,000 MWe-years of nuclear power. Approximately 160 m^3 of HLW glass and 1650 m^3 of TRU waste will be produced from reprocessing. By the year 2000, the volume of defense HLW, which is now stored in stainless steel tanks, will be more than 1000 m^3 [YANG-1987]. The HLW contains about 4.5 g/L aluminum, 30 g/L sodium, 13 g/L iron, 18 g/L uranium, and 4.8 g/L sulfate [WANG-1989].

Vitrification studies started in 1977 in China. A pot vitrification process similar to the PIVER process, using an induction-heated furnace at 1100-1150°C, was tested in a non-radioactive unit up to 1985. The pots/canisters were austenitic stainless steel and 120-137 mm in diameter by 739-920 mm long. Work was abandoned because of the low capacity of the pot system. China is currently developing a borosilicate glass vitrification plant using a two-stage continuous process similar to the German/Belgian Pamela or French AVM process. A nonradioactive full mock-up facility is being developed for startup in the mid-1990s, with a calciner throughput capacity of 50-55 L/hr producing glass at 40-45 kg/hr [LIU-1989]. The glass canister dimensions are 430 mm in diameter and 1335 mm in height. Control of ruthenium volatilization during waste evaporation and vitrification has been studied. Denitration during evaporation before vitrification using formic acid is preferred.

China's HLW streams have sufficient sulfate content to require special flowsheets to prevent separation of a sulfate phase in a joule-heated glass melter. Consequently, glass formulation efforts have been directed to glasses with 16-20% waste loading and the capability to incorporate sulfate with no resulting separation of a yellow sulfate phase. There is at least one report of a glass formulation additive being developed that eliminates the yellow phase separation in glasses to 20% waste loading with HLW containing up to 0.13 $\underline{M}$ SO_4^{2-} [SHANGGENG-1987]. The reported composition for this glass is given in Table B-2.

Borosilicate glass in stainless steel canisters is the first generation waste form but China is also considering conversion of HLW to SYNROC. A study is being undertaken with Australia on the feasibility of an active SYNROC demonstration plant in China, including investigation of possible disposal sites [NEI-12/88].

B.5 France

Nuclear Power Capacity (2000)	64 GWe
Reactor Mix	49 PWR; 4 GCR; 2 FBR
Reprocessing Plant Location	Marcoule, La Hague
Expected Glass Production (2030)	5400 m^3

France's entry into commercial production of electricity using nuclear energy began in 1956 when the Marcoule G1, a 2-MWe natural uranium, gas-cooled graphite reactor, was connected to an electrical grid. Based upon strong support by the nationalized electric utility, the gas-cooled graphite reactor design was discontinued in the late 1960s in favor of the Westinghouse PWR design. With the advent of the 1973 oil crisis, the government's energy planning was revised to include a substantial number of nuclear reactors using a standardized design, thereby starting a nuclear program leading to the present system of PWRs, GCRs and FBRs which produce 74% of the nation's electricity [GOLDSCHMIDT-1982].

France's policy on the back end of the nuclear fuel cycle is to develop complete domestic capabilities and to rely on industrial firms for conduct of fuel cycle operations as well as bear the associated costs. Reprocessing with recycle of uranium and plutonium is accepted as a necessary step in managing spent nuclear fuel. Plutonium and uranium are being recycled to a limited extent in both light-water reactors and breeder reactors. Uranium is being recycled to a small extent in light-water reactors [QUINAUX-1989].

Fuel cycle support (i.e., uranium supply, conversion, enrichment, fuel fabrication and reprocessing) is provided largely through Cogema, established in 1976 as an industrial firm wholly-owned by the CEA. The first five-year plan adopted by the government in 1952 established the Marcoule nuclear site, including a reprocessing plant for gas-reactor fuels; a second reprocessing complex was started by the CEA in 1959 near Cherbourg, France, for LWR oxide fuels, both domestic and foreign.

Table B-2. Glass Composition for HLW Solidification in China

Oxide	GP-12 Glass	HLW Oxides
Al_2O_3	2.5	1.70
B_2O_3	13.4	17.00
CaO	2.5	-
Cr_2O_3	-	0.11
Fe_2O_3	-	5.24
K_2O	-	0.02
Li_2O	3.4	5.00
MgO	1.5	-
MnO_2	-	0.04
Na_2O	4.0	5.07
NiO	-	0.08
PuO_2	-	0.01
SiO_2	46.2	43.40
SO_3	-	1.55
SrO	-	0.09
TiO_2	5.0	0.12
U_3O_8	-	4.73
ZrO_2	1.5	0.50
R.E. Oxides	-	0.75
HLW Oxides	20.0	2.00

Spent-Fuel Reprocessing

Gas-Cooled Reactor Fuels: Cogema reprocesses metal fuels from France's gas-cooled reactors, both domestic and foreign, in the 600 MTU/yr UP1 reprocessing plant located at the Marcoule Nuclear Industrial Center. High-level wastes are immobilized in borosilicate glass in the nearby AVM vitrification facility [LALLEMENT-1988; MARCOULE-1988]. By 1986, 16,500 MTU of GCR fuel had been reprocessed in France [NUMARK-1986].

Light-Water Reactor Fuels: Cogema reprocesses oxide fuels from both domestic and foreign reactors at the La Hague site on the northern coast of France. Two reprocessing facilities, UP2 and UP3, each with a capacity of 800 MTU/yr are located at the site. The UP2 plant has been operating since 1976 and UP3 started operations in late 1990. High-level wastes are immobilized in the R7 and T7 AVM-type vitrification plants located on the site [CHENEVIER-1987; LALLEMENT-1988].

Prior to transfer of all GCR fuel reprocessing to Marcoule, the UP2 plant at La Hague had processed about 4,900 MT of GCR fuel. By October 1990, the UP2 plant had processed more than 3,150 MT of oxide fuel; the UP3 plant, started in late 1990, processed 250 MT by the end of 1990 and is currently operating near the design capacity of 800 MT/yr [ROBINSON-1989].

LWR MOX Fuels: Loading of MOX fuel into LWRs in France began in 1987 at the St. Laurent reactor and has expanded to other LWR reactors but little has been reprocessed. During the recent improvements made to the UP2 reprocessing plant at La Hague, capability was added for reprocessing MOX fuels. Cogema's initial plans for reprocessing MOX fuels in the UP2 plant include MOX fuel from the German 340-MWe PWR at Obrigheim, probably in 1992; a 2-MT batch of MOX fuel was reprocessed in the APM/TOR facility at Marcoule in late 1990 [LENAIL-1988].

FBR Fuels: Reprocessing of FBR fuel from the Rapsodie FBR began on a laboratory scale at Fontenay-aux-Roses and continued in the one kg/day AT1 pilot reprocessing facility at La Hague until 1979 after processing more than one MT of Rapsodie fuel. Reprocessing of Rapsodie and Phenix FBR fuels began at Marcoule in 1975 using the 10-30 kg/day SAP/TOP pilot reprocessing plant; through 1987, 10.7 MT of FBR fuels had been processed in the facility and 9.9 MT of FBR fuel had been processed at La Hague, diluted with GCR fuel; in 1985, a new pilot reprocessing facility (APM) with a capacity of 5-7 MTHM/yr began radioactive operations at Marcoule on FBR fuels from Phenix; German SNR-300 FBR fuels are also scheduled to be processed through APM [LEFEVRE-1980; PATARIN-1987; LALLEMENT-1988].

HLW Immobilization

A pot vitrification process was first developed in France and installed in the Fontenay-aux-Roses R&D facility. In this process, glass frit and a gelling clay were fed into a melting pot together with the waste solution. Calcination proceeded in the heated pot while feeding was continued. After filling, the calcine was vitrified by further heating of the pot, and the glass was released into a storage container through a freezing valve in the bottom [BONNIAUD-1963]. After eleven years of research and development work, the vitrification studies were transferred to Marcoule in 1968 where the work was continued with highly radioactive waste solutions from the reprocessing plants in operation at Marcoule. An industrial pilot plant PIVER (Pilote Verre) was completed in 1967. Radioactive operation began in 1969 and 10 Mt of radioactive glass were produced by 1972 [BONNIAUD-1968, -1972]. Operation of PIVER was resumed in 1979 in order to solidify waste coming from the reprocessing of FBR fuel elements. After this program, PIVER was closed in 1980.

The successful operation of PIVER led to the construction of an industrial scale plant Atelier de Vitrification de Marcoule, AVM, using a continuous vitrification process. Inactive tests of components for AVM began in 1972 and the design of AVM, in 1973. The development of AVM has been reported continuously [JOUAN-1986; BONNIAUD-1975; REDON-1976]. Full operation was started in 1978 [DAMETTE-1985]. Equipped with one vitrification line, the facility has, by 1990, operated 50,000 hours and converted 1,443 m^3 of liquid wastes into 644 MT of borosilicate glass. The vitrified waste is contained in 1,841 metal canisters. Each canister holds 360 kg of glass and has a diameter of 50 cm.

Two AVM-type vitrification facilities are located at the La Hague reprocessing site in northwestern France. Each facility employs three processing lines and will convert 180 L/hr of liquid wastes into 60 kg/hr of borosilicate glass. The R-7 facility began operation in 1989 and is now vitrifying a backlog of HLLW from the UP2 plant. As of 1991, the R-7 facility has accumulated over 12,700 operating hours, producing 540 m^3 of glass in 548 canisters. The T-7 facility will begin operation in 1992 to vitrify HLLW from the UP3 plant.

A reference AVM glass called R7T7 (or SON 68) produced from LWR fuel reprocessing waste has been studied extensively in France. A composition is given in Table B-3. The intrinsic dissolution rate for this glass has been measured between 90°C and 250°C using a high-temperature Soxhlet apparatus [DELAGE-1991]. The dissolution rate was approximately 1 $g/(m^2 \cdot d)$ at 90°C and the activation energy was reported to be 60 kJ/mol. Long-term static corrosion tests have been performed in distilled-water [CAUREL-1991] and in the presence of smectite and montmorillonite clays.

The characteristics of the vitrified high-level wastes and the design of the waste canisters to be emplaced in a repository have been fixed by the on-going vitrification operations at La Hague and Marcoule. Still to be determined and the subject of R&D are glass durability in repository environments, the possible use of overpack containers, and the selection of barrier/backfill materials. Montmorillonite based clays, either in the form of pressed blocks or a loose form pressed around each waste canister, are being evaluated at Fontenay-aux-Roses for potential application as barrier/backfill material in a HLW repository [COULON-1987; BAUDIN-1988; BROC-1989; SCHNEIDER-1989]. To obtain data for the source term modeling of the wastes in a repository, France is carrying out considerable R&D directed at the dissolution of waste glass in groundwater containing dissolved minerals likely to be found in the geologic environment. Researchers at the CEA have reported on the development of an equilibrium/reaction path computer code for modeling geochemical and kinetic reactions of glasses in water which is very similar to studies in the U.S. using the EQ3/6 code. The effects of variations in glass composition are also being examined along with the behavior of natural basaltic glasses as a possible natural analogue for comparison with waste glass dissolution and model validation [CROVISIER-1989a, -1989b; GODON-1989; NOMINE-1989; PACAUD-1989; MUELLER-1990].

B.6 Germany

Nuclear Power Capacity (2000)	22.7 GWe
Reactor Mix	14 PWR; 7 BWR; 1 HTR; 5 East German reactors
Reprocessing Plant Location	La Hague, France; Sellafield, United Kingdom
Expected Glass Production (2030)	2500 m^3

Table B-3. Composition for R7T7 Reference Glass

Oxide	Wt %
Ag_2O	0.03
Al_2O_3	4.91
B_2O_3	14.02
BaO	0.60
CaO	4.04
CdO	0.03
Ce_2O_3	0.93
CoO	0.12
Cr_2O_3	0.51
Cs_2O	1.42
Fe_2O_3	2.91
La_2O_3	0.90
Li_2O	1.98
MnO_2	0.72
MoO_3	1.70
Na_2O	9.86
NiO	0.74
Nd_2O_3	1.59
P_2O_5	0.28
Pr_2O_3	0.44
Sb_2O_3	0.01
SiO_2	45.48
SnO_2	0.02
SrO	0.33
TeO_2	0.23
ThO_2	0.33
UO_2	0.52
Y_2O_3	0.20
ZrO_2	2.65

Germany's policy is to reprocess spent fuel and recycle plutonium. In 1989, the government and utilities elected to contract with foreign suppliers for reprocessing services. German utilities currently have approximately 8900 MT of reprocessing service contracted with Cogema in France and BNFL in the United Kingdom. Approximately 35 MT/yr of spent fuel will be treated and stored at the pilot conditioning plant (PKA) being built in Gorleben. Work is under way for transferring the high-level wastes from the once-proposed Wackersdorf (WAK) reprocessing facility in Karlsruhe to the Pamela facility in Mol, Belgium for vitrification. Vitrified high-level waste returned from the foreign reprocessors will be placed in interim dry storage for at least ten years prior to disposal along with spent fuel for which reprocessing is not economical.

Experimental work on the solidification of high-level radioactive waste was started in the mid-1960s. Krause [KRAUSE-1966] reported on German research on HLW solidification and indicated that these wastes should be converted into glass. Guber [GUBER-1970] gives references for the work performed prior to 1970. Development of a full-scale inactive testing facility, VERA, with a feed rate of 10-25 MT/h, began in 1965, and the device was built at the Nuclear Research Center in Karlsruhe [GUBER-1973]. A continuously operating process was used with a combination of spray calcination of the liquid waste, off-gas treatment, and a glass melting furnace with a freezing tube bottom outlet for casting. First runs took place in 1970. Borosilicate glasses were produced at melting temperatures of 1000°C. The operational experience obtained with this plant was used to plan a new vitrification facility, VERA 2. VERA 2 was designed for handling high-activity reprocessed waste but only a bench scale glass melting unit was actually built [RUDOLPH-1973]. Seven hundred kilograms of borosilicate glass were produced in the melting unit and the experience gained was used for the Pamela project (see Belgium). In 1977 all German activities in the field of high-level waste solidification were applied in a joint effort to develop and build the Pamela demonstration plant. With the transfer of the Pamela facility to Belgoprocess in Belgium and the demise of the Wackersdorf reprocessing plant, vitrification R&D will probably be curtailed in Germany.

One of the most significant contributions to modeling the chemistry waste glass/water interactions was carried out at the Hahn-Meitner Institute in Berlin. Grambow [GRAMBOW-1985] proposed a geochemical model based upon transition-state theory that explained the observed behavior of several different waste glasses in laboratory tests. The model developed by Grambow has been applied successfully to the study of natural basalt glasses from the deep ocean [GRAMBOW-1986a], alteration of basalt glass in seawater [CROVISIER-1986], and nuclear waste glass in contact with bentonite clay. A similar approach is being used to study the dissolution behavior of a French nuclear waste glass [ADVOCAT-1990] and has been integrated in a performance assessment model for a repository in Japan [McGRAIL-1990]. In the U.S., Bourcier et al. [BOURCIER-1990] has proposed a modification to the methodology suggested by Grambow to relate the affinity for glass dissolution to the affinity for the dissolution of a hypothetical alteration layer on the glass surface that consists of a mixture of various hydroxides and silicate phases. Although there are various nuances in each of these specific applications, it is clear that there is an international consensus on the use of the basic rate equation proposed by Grambow [GRAMBOW-1985] as the most successful theory for modeling glass/water reactions. Work is continuing in Germany to extend the applicability of this model to salt brines that are expected at the Gorleben site [GRAMBOW-1990].

B.7 India

Nuclear Power Capacity (2000)	1.7 GWe
Reactor Mix	14 PWR; 7 BWR; 1 HTR; 1 FBR
Reprocessing Plant Location	Tarapur, Trombay, and Kalpakkam
Expected Glass Production (2030)	400 m^3

India is placing heavy dependence on nuclear power to augment its electric power generating capacity. There is a three-phase program: (1) CANDU-type PHWR reactors fueled with natural uranium, (2) FBR's fueled with plutonium produced by first-phase reactors, and (3) self-sustaining thorium-uranium cycle reactors. The nuclear fuel cycle system will take advantage of the large thorium resources in India [MURTHY-1990]. India's policy on the back end of the nuclear fuel cycle is to reprocess spent fuels for recovery and reuse of nuclear materials. HLLW will be stored as acid in stainless steel tanks for 3-5 years after reprocessing and concentrated in an evaporator before vitrification [RAJAN-1986; MASTERS-1986]. The HLW glass is then stored for at least 20 years before disposal of in a deep geologic repository.

The Department of Atomic Energy (DAE) is responsible for all aspects of nuclear energy in India. DAE's major nuclear fuels complex is at Hyderabad. It has a uranium refining and conversion facility, a fuel fabrication facility, a zirconium fabrication facility, a fuel assembly components production facility, and a fuel assembly facility. DAE has a uranium refining and conversion facility at Trombay, fuel reprocessing facilities at Kalpakkam, Tarapur and Trombay, and a plutonium fuel fabrication facility for FBRs. The Nuclear Power Corporation is responsible for design, construction, and operation/maintenance of nuclear power stations. The Tarapur atomic power station includes a pilot-scale fuel reprocessing plant and a HLW vitrification plant. The Kalpakkam (Madras) nuclear power station includes a pilot-scale fuel reprocessing plant and a future HLW vitrification plant.

The Bhabha Atomic Research Center (BARC) at Trombay, Bombay carries out fuel cycle, waste vitrification and disposal R&D, and R&D on uranium ore processing [MURTHY-1988]. BARC has five test reactors and a number of pilot-scale facilities for isotope production and processing, fuel reprocessing, fuel materials production, HLW vitrification, and treatment of alpha-emitting wastes (incineration, wet oxidation), immobilization of fuel cladding hulls, and decommissioning. The Indira Ghandi Centre for Atomic Research (IGCAR) at Kalpakkam carries out fuel cycle R&D, including FBR fuel reprocessing and waste management. IGCAR has an interim storage facility for vitrified HLW, a fast breeder test reactor, and a thorium-fueled test reactor (Kamini reactor, 30 kW). A nuclear science center was established at the University of Madras in 1989 with linkage to IGCAR.

Research on solidification of HLW has been undertaken at BARC since the early 1960s. Currently, development of a joule-heated melter is underway for use in future higher-capacity needs [RAJ-1989]. A 10-year program of vitrified waste storage in experimental storage assemblies simulating repository conditions is in progress. Samples of wastes are taken periodically for examination and testing. One test canister is in a granite block [SAMUEL-1987]. A major program is being carried out in which detailed characteristics of the vitrified HLW are evaluated. An extensive materials tests program is being carried out at Tarapur to evaluate long-term characteristics of solidified high-level radioactive waste products under extended storage/disposal conditions. The tests include engineering-scale waste packages with simulated and actual HLW.

The remotely operated and maintained WIP facility (Waste Immobilization Plant) at Tarapur is used to convert HLW at Tarapur to borosilicate glass [RAJ-1989; SAMUEL-1989]. Construction was completed in 1981 and "warm" commissioning tests were completed in 1985-1986. The plant is designed around the "pot-glass" process where HLW is calcined at 600 °C in a metal melter vessel until the melter vessel is about 75% full. The calcine is then melted at 950-1000°C in the same melter vessel. Heating is with a three-zone induction furnace. The Inconel-690 melter is 0.325 m in outside diameter and is 1.8 m long. The melter is drained through a drain pipe (freeze valve) into a stainless steel canister that is insulated to retard cooling. The 304-L stainless steel canisters are 0.325 m in outside diameter by 0.775 m high (wall thickness is 10 mm), and contain 125 kg in 45 liters of glass (27 wt% waste oxides) in a canister. The heat generation rate in a canister is up to 1.75 kW. After sealing the canister by automatic welding of the lid, the canisters are inserted into a carbon steel overpack, the lid is welded on, and the overpack (with two canisters) is taken to the interim storage facility. The process capacity is 25 liters/hr (600 liters/d) of HLW processed combined for the two process lines, producing one canister/day. Each of the two calcining/melting furnaces is rated to produce 4 kg/hr of glass. A reference canister will contain about 94,000 curies and an estimated 393 W of heat initially.

The WIP facility at Trombay will be used to vitrify HLW from the Trombay reprocessing plant into borosilicate glass [RAJ-1989]. The process is similar to the one at Tarapur, but of advanced design. The WIP facility at the IGCAR at Kalpakkam will be used to vitrify HLW from the Kalpakkam reprocessing plant (spent fuel from the Madras Atomic Power Station, from the FBTR, and the future prototype fast breeder reactor, PFBR), into borosilicate glass [RAJ-1989]. The process and facility is again similar to the one at Tarapur, but of advanced design.

Vitrified HLW is to be interim stored for 20-25 years to cool the vitrified waste, to ensure the integrity of the waste package before disposal, and to facilitate safe handling and transportation of the vitrified HLW to the repository. Vitrified HLW from Tarapur and Trombay reprocessing facilities are to be stored in engineered facilities with stack-induced (the stack is 100 m high) natural-draft air cooling.

India has not yet developed a reference geologic disposal concept. Current considerations are for reference vitrified HLW borosilicate glass containing up to 27% waste oxides. Vitrified HLW canisters have a diameter of 375 mm and are 0.375 m long. Each contains about 125 kg of glass and the initial heat output is about 2.5 kW [RAJAN-1983].

B.8 Italy

Nuclear Power Capacity (2000)	1.1 GWe
Reactor Mix	1 PWR; 1 BWR
Reprocessing Plant Location	Trisaia
Expected Glass Production (2030)	600 m^3

When Italy was using nuclear power, the policy was to develop indigenous fuel cycle and waste treatment capability but purchase all enrichment and conversion services. In 1988, the National Energy Plan (PEN) called for the abandonment of nuclear power and increased use of coal and natural gas for electricity generation. Since February 1989, Italy has been under a five-year moratorium against operating or constructing nuclear power reactors. Italy continues research into nuclear energy but with a reduced R&D budget. Italy plans to store spent fuel and reprocess only if there is a need for plutonium. An Italian production plant for reprocessing has currently been abandoned, but if decided upon, it will not be needed before about the year 2000. Future reprocessing, if any, is expected to be with foreign projects.

The Italian Commission for Nuclear and Alternative Energy Sources (ENEA) is responsible for nuclear research and development, waste treatment and immobilization, waste isolation, nuclear safety and control, nuclear facility decommissioning, and protection of health and environment. The ENEA's Energy Research Center at Casaccia conducts nuclear fuel cycle R&D and has a HLW glass characterization lab [CERRETTI-1987; COSTA-1987; DE CRESCENZO-1987]. The ENEA's Energy Research Center at Saluggia conducts fabrication and reprocessing of fuel elements. The EUREX pilot plant (30 kg/d) at Saluggia was originally designed for MTR fuels, then modified for CANDU fuels (to 1983) and currently being modified for MOX fuels. The scheduled shutdown is in 1995 [ALONZO-1984; POZZI-1987]. The ENEA's Trisaia Energy Research Center develops fuel reprocessing and waste vitrification technology. The ITREC pilot plant at Trisaia (5 MTU/yr) is currently testing innovative components for future industrial reprocessing plant. At this center is the IVET-1 nonradioactive HLW (rising-level pot) vitrification pilot plant (20 liter/hr feed rate) and the IVET-2 radioactive HLW (rising-level pot) vitrification pilot plant (planned startup late 1990s) [COSTA-1987]. Italy's GCR fuel is sent to the U.K. for reprocessing.

Glass Production

The "ESTER" in-pot vitrification process was tested in the nonradioactive pilot plant IVET-1 at Trisaia since 1984 and in hot cell tests at CEC's ISPRA laboratory [RISOLUTI-1983]. The "ESTER" process was shut down in 1985 and replaced by the "PETRA" pot vitrification process (with mini-reprocessing). "PETRA" is expected to operate from 1987-1991. EUREX has about 100 m^3 of assorted HLW. ENEA is considering treatment by separation and cementation of inert ingredients and by vitrification of fission products by pot process. The French AVM process has been designed for EUREX wastes but a decision on its use has not yet been made. The estimated plant cost is $80 million (U.S.). Vitrified HLW from the foreign reprocessing plant will be returned to Italy and stored for 50 years or longer before being placed in a geologic repository [NEGRONI-1986].

The Commission of the European Communities (CEC) Joint Research Center - ISPRA Establishment located in northern Italy and conducts coordinated research on HLW solidification and waste management studies for European communities. Italy is studying the HLW "declassification" concept to remove actinides and radiocesium and radiostrontium for vitrification in IVET or PETRA. The remaining waste stream would be cemented as LLW/ILW [MATALONI-1987]. Progress has been reported on a declassification (selective separation) chemical process that was developed and tested to drastically reduce the volume of vitrified product [VENDITTI-1989]. Extensive lab-scale experimental activity has been carried out under a contract with Lowenberg Associates-Battelle PNL to select the proper declassification (selective separation) chemical process for HLW [VENDITTI-1989]. Australia signed an agreement on SYNROC research with Italy's ENEA to evaluate the sol-gel technology (developed in Italy) as a route for precursor powders for SYNROC production. The Center for Advanced Technologies (CETA) near Bologna produces gel-supported precipitation precursors for use in SYNROC HLW immobilization. Studies are continuing on long-term waste isolation performance and disposal safety [CHAPMAN-1985a, -1985b]. A study of interaction with the disposal environment (clays) has been performed in cooperation with the Belgian SCK-CEN [VENDITTI-1989].

Two different glasses have been studied in Italy. The composition of the reference BEL-15 glass is shown in Table B-4. The reference BEL-15 glass has been formulated for the direct vitrification of aluminum rich HLW. Extensive studies have been made on BEL-15 glass behavior with reference to the underground disposal in a clay formation. The BEL-15 glass has been leach tested in experiments with two types of clays (Italian and Belgian) and insitu experiments at the Mol underground research laboratory. Overall, the BEL-15 glass has shown good characteristics comparable of the other European glasses. A second glass formulation, named BAZ, has been developed for the "declassification" option, since the waste to be vitrified has an unusual composition (zeolites plus iron and aluminum hydroxides).

B.9 Japan

Nuclear Power Capacity (2000)	50.8 GWe
Reactor Mix	23 PWR; 26 BWR; 1 GCR; 1 ATR; 1 FBR
Reprocessing Plant Location	Rokkasho-mura
Expected Glass Production (2030)	4400 m^3

In Japan, government responsibilities for the establishment, operation and inspection of nuclear facilities are shared between the Science and Technology Agency (STA), the Ministry of International Trade and Industry (MITI), and the Ministry of Transport. The various government bodies work closely with Japanese heavy industry companies in all aspects of the nuclear fuel cycle. MITI has general responsibility for promoting and coordinating industrial activity in nuclear energy and the fuel cycle. The Central Research Institute of Electric Power Industry (CRIEPI) reports to MITI and provides R&D support for Japanese utilities, including waste management R&D in the areas of transportation, storage, and disposal of HLW. The Japan Nuclear Fuel Service Company (JNFS) is in charge of commercial reprocessing, including solidification and interim storage of reprocessing wastes, and the construction and operation of storage facilities for wastes returned from foreign reprocessors of Japanese spent fuel.

Table B-4. Reference Chemical Composition of the Borosilicate Glass BEL-15 [VENDITTI-1989]

Oxide	wt %
Al_2O_3	12.89
B_2O_3	17.00
CaO	8.93
Cs_2O	0.46
Fe_2O_3	0.20
Li_2O	5.00
Na_2O	10.67
SiO_2	43.40
SO_3	1.21

The STA has jurisdiction over the Power Reactor and Nuclear Fuel Development Corporation (PNC), the Japan Atomic Energy Research Institute (JAERI), and the Radiation Council (which establishes technical standards for radiation protection). The PNC and JAERI share government reservations at the Tokai-mura and Oarai-machi Research Establishments. The PNC was formed in 1967 and is the main channel for the development and demonstration of fuel cycle technology, including HLW and transuranic waste management. The JAERI was established in 1956 and also performs research for HLW waste management. The Government Industrial Research Institute, Osaka (GIRIO) performs R&D into alternatives for HLW solidification, and waste-form characterization. Hitachi Engineering Co., Ltd., develops technology to store and reprocess spent LWR fuel, store, fix and dispose of HLW. Ishikawajima-Harima Heavy Industries Co., Ltd. (IHI) is a private company responsible for the development of a nuclear waste management system. The JGC Corporation is a private corporation responsible for the design and construction of fuel reprocessing and radioactive waste treatment facilities and performs waste management R&D, including wet oxidation, incineration, waste forms, ash melting, and selective nuclide removal. Kobe Steel, Ltd., is a private company that has activities in spent fuel transportation and storage cask design and production, waste treatment equipment and systems, and HLW handling and storage. The Mitsubishi Metal Corporation (MMC) is a private company that performs design and research on facilities for spent fuel storage and reprocessing, waste treatment, and geologic disposal.

Reprocessing of spent nuclear fuel is an integral part of the nuclear fuel cycle in Japan, followed by eventual recycle of fissile materials [OECD/NEA-1988; OYAMA-1989]. Japan has been reprocessing in the small plant at Tokai-mura, but most reprocessing is currently contracted to other countries until larger capacity is available in Japan. Consideration will be given on whether or not to extend reprocessing consignments with overseas facilities after the year 2000.

Japan currently has foreign contracts for reprocessing 5,900 MTU with BNFL (U.K.) and COGEMA (France). Plutonium derived from this activity will be returned to Japan by sea, beginning in 1992 at the earliest. A small-scale (210 MT/yr) domestic reprocessing plant began operations in September 1977 at Tokai-mura. This plant had processed 509 MT of spent fuel by the end of 1990. PNC is considering converting the Tokai plant to an experimental facility to study FBR fuel reprocessing once the planned Rokkasho reprocessing facility begins operating.

JNFS plans a commercial reprocessing plant with a capacity of 800 MTU/yr at Rokkasho-mura [TSUBOYA-1989], with startup in October 1998 processing LWR spent fuel. This plant will use technology developed primarily in France, with input from Japanese, British, and German companies, and will include about 3000 MTU wet storage of spent fuel. The plant will be built on a 700-acre site at a cost of 840 billion yen ($6.5 billion). Startup was originally planned for 1997, but has recently been delayed for 10 months.

Glass Production

Japan is building a 38-billion yen ($300-million) demonstration vitrification facility at Tokai-mura (Tokai Vitrification Facility, TVF) capable of vitrifying 0.35 m^3/d of concentrated HLW (216 kg/d glass production rate) [YOSHIOKA-1989]. The Tokai Vitrification Facility (TVF) began hot operation testing in 1991. Plant operation at a nominal glass production rate of 9 kg/hr is scheduled for 1992. A larger-scale vitrification and storage facility for HLW is planned at the Shimokita site in Aomori prefecture, to treat HLW from the reprocessing plant to be built there [TSUBOYA-1989].

The TVF has two stories underground and three above ground, with a floor space of 2,600 m^2, to handle waste from the reprocessing plant. Glass-making additives for the TVF will be supplied to the melter in the form of glass fiber cylinders 70 mm in diameter. Canisters of vitrified HLW (110 liters of glass weighing 300 kg) will be stored at Tokai during a 30-50 year cooling period and then disposed of in the proposed geological repository. The Japanese-designed stainless steel canisters will have a different design but the same overall dimensions as those to be received from France and the U.K., but the Japanese canisters will contain 110 liters of glass instead of 150 liters for the French and U.K. canisters. Final melter design parameters are [YOSHIOKA-1989]: (1) operating temperature 1100 ± 50°C, max. 1250°C; (2) produces 8.8 kg/hr of glass from 15 L/hr of conditioned HLLW (150 g/L oxide) and 6.6 kg/hr glass fiber additive; (3) bottom-drain discharge of vitrified HLW every 34 hr; (4) operating lifetime 5 years; (5) dimensions 1.9 x 1.9 m x 2.3 m high; and (6) melting surface area 0.66 m^2, maximum glass holdup volume 350 L.

HLW from reprocessing will be concentrated to a composition equivalent to 0.5 m^3/MTU before transfer to the glass melter, using a continuous feed system with a two-step computer-controlled airlift [TSUBOYA-1989]. The joule-heated ceramic melter is based on the glass melter used commercially in the glass industry, but with modifications and improvements added by PNC to make it more suitable for HLW vitrification. These include changes in glass pool design to prevent the accumulation of electroconductive sludge, use of a glass-fiber additive to reduce particulate entrainment in the off-gas system, improved instrumentation including a glass level detector, remote operation, and design to permit easier dismantling of the highly-radioactive melter after 5 years of operation [YOSHIOKA-1989].

Future dismantling of the joule-heated ceramic melter for vitrification of HLW at the Tokai Vitrification Facility has been studied. The melter is expected to have a life of only 5 years, so a mock-up melter was dismantled to obtain data. The total time required to dismantle the simulated radioactive melter was 361 hours, generating 40-50 containers or 340 liters volume of waste weighing 600 kg [OGATA-1989].

The final vitrified waste composition will be 75% glass additives (43-47% silica) with 25% of HLW in oxide form. A reference simulated waste glass composition used in current glass testing programs by PNC is given in Table B-5.

PNC has studies underway to clarify the fundamental behavior of engineered barrier materials under repository conditions. These studies involve glass form leaching tests, candidate overpack corrosion tests, buffer material long-term stability evaluations, radionuclide migration studies, and acquisition of thermodynamic data on radionuclides and minerals [TSUBOYA-1989]. Natural analogs, such as natural basaltic glass, are being used to evaluate the long-term behavior of multiple engineered barriers in HLW repository systems. Sample ages of 280 and 2,800 years were simulated, and leaching rates determined. Volcanic glass, smectite-illite deposits, old concrete and old steel pipes were examined to estimate the long-term stability of engineered barrier materials [SASAKI-1990].

Vitrified HLW, and potential overpack and buffer materials are being examined as part of a long-term plan for engineered barrier development. Static tests are being conducted with fully radioactive vitrified HLW. Full-scale overpacks of forged carbon steel and porcelain are also being fabricated and tested. Properties of sodium bentonite clay are also being measured.

Table B-5. Composition of Simulated Waste Glass P0798

Oxide	wt %	Oxide	wt %
Al_2O_3	5.00	NiO	0.23
Ag_2O	0.02	P_2O_5	0.30
B_2O_3	14.20	PdO	0.35
BaO	0.49	Pr_6O_{11}	0.42
CaO	3.00	Rb_2O	0.11
CdO	0.02	Rh_2O_3	0.14
CeO_2	3.34	RuO_2	0.74
Cr_2O_3	0.10	SeO_2	0.02
Cs_2O	0.75	SiO_2	46.60
Eu_2O_3	0.05	Sm_2O_3	0.29
Fe_2O_3	2.04	SnO_2	0.02
Gd_2O_3	0.02	SrO	0.30
La_2O_3	0.42	TeO_2	0.19
Li_2O	3.00	Y_2O_3	0.18
MnO_2	0.37	ZnO	3.00
MoO_3	1.45	ZrO_2	1.46
Na_2O	10.00	Nd_2O_3	1.38
TOTAL	45.65		54.35

B.10 Netherlands

Nuclear Power Capacity (2000)	0.4 GWe
Reactor Mix	1 PWR; 1 BWR
Reprocessing Plant Location	France and the U.K
Expected Glass Production (2030)	45 m^3

In 1985, the Netherlands initiated an Integrated National Research Programme (ILONA) to study storage and disposal of LLW, ILW, and HLW in deep geological formations in the Netherlands, disposal in the sub-seabed sediments (supervised by the Deep-Sea Research Programme on Radioactive Waste, DORA Committee), and disposal in a multinational repository in another country. The COVRA (Central Organization for Radioactive Waste), founded in 1982, is the only organization authorized to collect, treat, transport and store (and dispose of) LLW/ILW in the Netherlands [CODEE-1987]. The ECN (Petten Research Center of The Netherlands Energy Research Foundation) carries out energy studies, radioactive waste treatment and disposal studies, decontamination studies, and other nuclear research [LEIGH-1990]. The Hot Cell Laboratory (HCL) is the only facility in the country for investigation of large, highly-radioactive materials. The KEMA (Research and Testing Electrochemical Materials Company) at Arnhem carries out research and engineering services for utilities, including R&D on volume-reduction and storage of reactor station wastes [LEIGH-1990].

In 1985, the Dutch government agreed in principle to the possible future construction of additional nuclear power plants. However, because of the public's concern about nuclear energy since the Chernobyl accident in 1986, the Netherlands has deferred any possible new construction of nuclear power plants. Consequently, the government has contracted with France for reprocessing of 120 MTU of spent fuel and with the U.K. for another 45 MT. Long-term reprocessing plans are uncertain. HLW from spent fuel reprocessed in France and the U.K. will be vitrified into borosilicate glass at the foreign reprocessing facilities and returned to the Netherlands for final disposition starting in 1994 [CODEE-1989]. Total arisings of HLW from foreign reprocessing will be approximately 20 m^3/yr of vitrified HLW for a cumulative total of about 45 m^3, and a total of about 500 m^3 of non-heat-generating HLW.

The Netherlands is to provide for interim storage of spent fuel and all radioactive wastes, including vitrified HLW and other reprocessing wastes returned from foreign reprocessors, until disposal can be accomplished. Extended storage of the wastes for 50-100 years is planned in a central engineered facility, about one km from the Borssele nuclear power plant, and such storage and subsequent disposal is managed by the government. Central storage should be implemented by 1994 at the latest [CODEE-1989]. The Netherlands is seeking foreign disposal of its HLW, but continues with a domestic program to site and develop technology for a geologic repository in a Dutch salt formation.

B.11 Switzerland

Nuclear Power Capacity (2000)	3.8 GWe
Reactor Mix	3 PWR; 2 BWR
Reprocessing Plant Location	France and the U.K.
Expected Glass Production (2030)	1200 m^3

The Swiss government has contracted with France and the U.K. for reprocessing of spent fuel to be discharged up through 1993 [ROMETSCH-1986]. Reprocessing of 165 MTU spent fuel has been contracted to BNFL and 599 MTU to COGEMA. The current estimates of HLW arising from the reprocessing contracts abroad are 240 m^3. Receipt of vitrified HLW from foreign reprocessing is expected to begin in 1993. The National Cooperative for the Disposal of Radioactive Waste (NAGRA) had planned storage and repository capacity around a reference 240 GWe generating capacity over 40 years giving rise to 1200 m^3 glass (6000 canisters) or 3700 m^3 spent fuel (7860 MT) [NAGRA-1985]. Planning as of 1988 is based on 160 GWe total.

The policy on the back end of the nuclear fuel cycle in Switzerland is to purchase foreign reprocessing services for spent fuel and recycle plutonium to either LWRs or FBRs. The option is open for direct disposal of spent fuel. The policy is to store vitrified HLW and spent fuel that is not reprocessed in a central AFR facility (in dry casks) until it is reprocessed or disposed of (not before 2020). Plans are to store LLW and ILW in separate halls at the same storage site until a disposal facility is available. HLW and alpha wastes are to be disposed in a deep crystalline rock repository. The preferred option is to dispose of HLW and alpha wastes in other countries. Discussions have been held with China to reprocess some Swiss spent fuel and to keep the wastes.

A project for a central facility (called ZWILAG) was initiated for interim storage of spent fuel and reprocessed wastes. It will use a dry cask system and completion of licensing is expected in 1994. The facility is to be located adjacent to the Paul Scherrer Institute at Wurenlingen. The facility will have a capacity for 1555 MTU of spent fuel or 550 m^3 of vitrified HLW from reprocessing of 4968 MTU of spent fuel in 184 casks. This initial capacity is sufficient for 15-20 years accumulation. Future capacity is planned for 30-50 years accumulation. The facility will also provide separate storage halls for LLW and ILW. The owners of the two Beznau power plants applied for an interim onsite storage facility for spent fuel, vitrified wastes, and other wastes. Depending on progress of the central storage facility, only part of the Beznau storage facility may have to be constructed [NEA-1/90].

NAGRA has responsibility for siting, design, and operation of waste management facilities. It also carries out waste management R&D. NAGRA has operated an underground research laboratory (URL) in crystalline rock at Grimsel Pass since 1984. Utilities will provide central storage for vitrified HLW, other reprocessing wastes, and spent fuel. Other nuclear waste R&D organizations include the Paul Sherrer Institute (PSI), the Federal Interagency Working Group on Nuclear Waste Management (AGNEB), and the Commission on Nuclear Waste Management. R&D at PSI includes the characterization of waste matrixes (glass, concrete, bitumen), repository performance, and radionuclide transport in the geosphere and biosphere.

To demonstrate the technical feasibility and long-term safety of radioactive waste disposal in Switzerland, generic repository safety analyses and construction project studies (Project Gewahr) have been performed [ISSLER-1985; NAGRA-1985]. *In situ* tests are being performed in the URL at Grimsel Pass in northern Switzerland [THURY-1985].

The reference waste is HLW in borosilicate glass cooled 40 years after reactor discharge. It contains about 10 wt% actinide and fission-product oxides. The reference waste package concept is HLW borosilicate glass in a stainless steel canister with a thick, sealed cast steel disposal container overpack of wall thickness 25 cm, total length of 2.0 m, and outside diameter is 0.94 m. The design life is 1000 years. Maximum temperature of the emplaced HLW glass is about 195°C and the disposal container is about 150°C. Packing/buffer and seal materials are compacted bentonite (>1 m thick) is emplaced around HLW packages to fill tunnels.

The Swiss have cooperative agreements with Sweden (SKB), France (CEA/ANDRA), Finland (TVO and IVO), Japan (PNC), the FRG (BMFT, BGR, GSF), Belgium (ONDRAF), and the U.K. (NRPB, BGS, BNFl) on radioactive waste management. Joint Swiss-Swedish-Japanese leaching tests were conducted on French and British AVM glass samples.

B.12 England (United Kingdom)

Nuclear Power Capacity (2000)	12.8 GWe
Reactor Mix	24 GCR; 14 AGR; 1 HWR; 1 PWR
Reprocessing Plant Location	Sellafield
Expected Glass Production (2030)	1600 m^3

The nuclear industry in the U.K. has been highly nationalized, with responsibilities assigned to various government-supported agencies and corporations reporting to different government ministries or departments. AEA Technology, a government agency under the Department of Energy and formerly the United Kingdom Atomic Energy Authority, is responsible for nuclear research, which includes nuclear fuel cycle and radioactive waste management technology development. British Nuclear Fuels plc (BNFL), a government-owned corporation under the Department of Environment, provides commercial fuel cycle services for domestic and foreign customers including reprocessing of spent fuel and management of high-level wastes from reprocessing [BNFL-1988; JOHNSON-1990].

The U.K. operates six generic types of reactors producing spent fuel: (1) the Magnox reactors; (2) the AGRs; (3) the future PWR LWR, Sizewell B; (4) the SGHWR at Winfrith; (5) the PFR at Dounreay; and (6) the materials test reactors (MTRs). The 24 CO_2-cooled, graphite-moderated Magnox reactors vary in size from 60 MWe to 655 MWe each. A fuel assembly, or pin, consists of natural uranium metal clad in a magnesium alloy (Magnox) and varies in length from 74 to 110 cm and in diameter from 2.9 to 5.0 cm. The burnup of the fuel ranges from less than 4000 to 5400 MWd/MTU [NEI-11/90]. The 14 CO_2-cooled, graphite-moderated Advanced Gas Reactors (AGR) are of one size--660 MWe each; fuel assemblies contain 36 pins each, fabricated of UO_2 clad in stainless steel of about 100 cm in length. Enrichments vary from 2.11 to 2.77% and the fuel is irradiated to 18,000 to 21,000 MWd/MT [NEI-11/90].

The U.K.'s strategy for spent fuel management revolves heavily around fuel reprocessing. BNFL reprocesses Magnox fuels (uranium metal clad in magnesium alloy) at Sellafield and is constructing a reprocessing plant (THORP) for AGR and PWR fuels at Sellafield. The UKAEA operates reprocessing facilities for materials testing and fast reactor fuels at Dounreay in northern Scotland. Both sites service domestic and foreign customers.

Because of fuel cladding corrosion in water storage, Magnox fuels must be reprocessed soon after irradiation (within 6 to 12 months) or moved into dry storage, which allows a longer storage period (i.e., several years). A dry storage facility has been built at Wylfa for Magnox fuels. AGR fuel cladding, while more durable than that of Magnox fuels, also suffers from corrosion in water, and wet storage is limited to about 3 years. Dry storage of AGR spent fuel is also being considered to provide more flexibility in planning reprocessing campaigns. The capacity of the water basin at the one PWR LWR under construction is sufficient for 18 years of operation [WILKINSON-1987; SILLS-1989].

The U.K. has developed major fuel reprocessing facilities at Sellafield for gas-reactor and light-water reactor fuels and a small facility for reprocessing materials testing reactor and breeder reactor fuels at Dounreay [NEA-1990]. High-level liquid wastes resulting from reprocessing activities are stored in stainless steel tanks contained in concrete vaults until they can be fed to the vitrification facilities.

Processes for the vitrification of liquid high-level wastes have been studied since the U.K.'s nuclear program began. The original FINGAL work (in-canister batch melting and conversion to glass) was completed in the 1960s. Development resumed in 1972 with the intention to implement the vitrification at Sellafield based upon the newer pot-type HARVEST process. A comparison of the HARVEST process and the French AVM process in 1979-80 led to a decision by BNFL to adopt the AVM process based upon its advanced development and higher throughput. Construction of the Windscale Vitrification Plant (WVP) was completed and commissioning started in 1989. Radioactive operation began in 1990 on Magnox waste [HEAFIELD-1989].

The French AVM process adopted for use at Sellafield employs a continuous rotary inclined-tube calciner and an elliptical cross-section metallic melter. Two lines have been installed that are capable of vitrifying the high-level wastes from 2500 MT of Magnox fuel per year and producing 600 canisters per year, each containing 150 liters of glass [HEAFIELD-1989]. The product canisters are 430 mm in diameter by 1340 mm high and are fabricated of Type 309 stainless steel. Each canister contains 150 liters of borosilicate glass (20 wt% waste oxides) and weighs 470 kg. The maximum heat output is 2.5 kW [HEAFIELD-1989].

The current national strategy for HLW involves the use and development of a range of treatment/conditioning, storage and disposal facilities and a continuing program of research and assessment to ensure that the waste is disposed in the most appropriate way [DOTCHIN-1988; FLOWERS-1989; NEA-1990]. High-level wastes will be stored at Sellafield and Dounreay adjacent to the reprocessing facilities where they are generated. Storage for at least 50 years is anticipated [WILKINSON-1985]. The 50-year period will start with the commissioning of the THORP reprocessing plant, expected in 1992 [NEA-1990]. After this period a decision will be made as to their disposal as HLW or ILW.

The U.K., as part of its long history of nuclear activities, has conducted an extensive amount of R&D on waste conditioning, storage and transport. Considerable R&D on HLW vitrification is directed mainly at optimization of the French AVM-type processes being installed at Sellafield.

B.13 Soviet Union (Former)

Nuclear Power Capacity (2000)	100 GWe
Reactor Mix	21 RBMK; 25 VVER (PWR); 2 BWR; 2 FBR
Reprocessing Plant Location	Kyshtym
Expected Glass Production (2030)	1200 m^3

The Ministry of Atomic Power and Industry (Minatomenergoprom or MAPI, the combination of the Ministry of Medium Machine Building and the Ministry of Nuclear Power) is responsible for the civilian and defense nuclear fuel cycle, reprocessing, and waste-management operations. The Chemical Plant Research Institute in Sverdlovsk carries out R&D on HLW vitrification. The V. G. Khlopin Radium Institute, located in Leningrad, does R&D on radioactive wastes and geologic disposal, reprocessing, partitioning, gases from radiochemical plants, organics from radioactive waste, and radiation sources using cesium (in phosphate glass) and strontium (in borosilicate glass). The Radon facility established in 1964, located near Zagorsk (about 100 km east of Moscow), also conducts feasibility and demonstration studies on the vitrification of low- and intermediate-level radioactive wastes.

The Soviet policy on fuel reprocessing has been to recover and recycle uranium and plutonium. However, reprocessing of RBMK fuel has not yet been started, and no decision has been made on its ultimate disposition [BRADLEY-1990]. Reprocessing of defense reactor fuel began in 1949 at the Kyshtym site with a process involving sodium uranyl acetate precipitation from nitric acid solution. The current method uses the PUREX process [DROZHKO-1989]. Reprocessing of commercial reactor fuel is reported to have started in 1978 at Kyshtym on VVER-440 and on naval reactor fuel. Over the plant's 10 years of reprocessing, about 2000 MTU of civilian reactor fuel were processed [BRADLEY-1990]. A large reprocessing facility near Krosnoyarsk was 30% complete by July 1989. Construction of this plant was indefinitely postponed in the summer of 1989. This facility was to have been built in increments with a capacity of 1500 MTU/yr.

As of 1990 in the Soviet Union, about 11,000 MT of spent fuel will have been discharged from all VVER (including those in other CMEA countries) and RBMK reactors. An estimated 30,000 MT of spent fuel will be discharged by the year 2000. The quantities of wastes generated by reprocessing 1 MT of spent fuel are: 0.7 to 1.0 m^3 high-level liquids; 3 to 5 m^3 intermediate-level liquids; and 50 to 100 m^3 low-level liquids [GKAE-1978]. The liquid wastes from reprocessing are vitrified into a final volume of 100-150 L/MTU [SEDOV-1983, -1988]. Three canisters, each containing 200 L of glass, are placed in a larger container and will be kept in air storage for 30-50 years.

Vitrification R&D

Solidification research on high-level wastes started in the 1950s. Phosphate and borosilicate glasses, "vitromet" and metal matrix, and ceramics (including "synthetic minerals") were or are being studied. Calcination processes such as fluidized bed, spray calciners, and rotary evaporators have been studied. Induction-heated batch and continuous ceramic melters have also been studied. HLW glasses have been produced in a single-stage ceramic melter. Crystalline HLW forms have been produced using a calciner and an induction-heated melter [KEDROVSKIY-1987; NIKIFOROV-1988].

Several pilot-scale vitrification plants using nonradioactive simulated wastes and/or using radioactive wastes as feed materials have operated, including one capable of processing 100 L/h of glass that had operated for 10 years as of 1987. A fully radioactive single-stage solidification process using a ceramic melter operated at Kyshtym from 1987 to 1988 and produced about 160 MT of phosphate glass containing 3.9×10^6 Ci. After 13 months of producing phosphate glass, the furnace was decommissioned because of "loss of tightness" (corrosion) of the system used to cool the leads to the melter electrodes.

In 1989, the design of a new two-stage melter system was completed and was expected to be operational in 1991. The process is based on a method to dry the liquid waste and then melt the waste in a second stage using a high-frequency induction melter [NIKIFOROV-1990]. A "cold-wall" or cold-crucible" design helps to contain the melt and decrease corrosion of the melter materials. The design capacity is 100 L/h of feed solution and 25-35 kg/h of solidified product.

Pilot processes, including both ceramic and induction melters were initiated at the Radon facility in mid-1989 for vitrification of ILW. Production rates were 100 kg/h of glass with a liquid-waste feed rate of 300 L/h. A plasma-jet fuel burner based on an electric-arc plasmatron was also identified as a promising method. Relatively high temperatures (1500°C) are used during LLW/ILW processing to obtain highly stable mineral slag. High temperatures also make it possible to incinerate unsorted wastes and wastes with up to 30% metal and 10% concrete.

Significant R&D on partitioning of HLW streams into various fractions has been conducted. A pilot plant has separated about 300,000 Ci each of cesium and strontium [ALOY-1989]. Research is being conducted on separation or partitioning of element fractions from HLW using cobalt dicarboly anion in strong HNO_3. This reagent is especially effective for large ions. The process separates strontium, cesium, rare earths, and transuranic elements with efficiencies up to 99%. The waste products are vitrified into glass blocks or glass-metal composites. The use of transmutation for treatment of certain radioactive element fractions is also being studied. After separation into fractions containing actinides, fission products, and/or isotopes of long half-life, the fractions would be fabricated into targets and irradiated in a high flux of thermal neutrons, or protons. In the case of neutron irradiation, a mixture of lithium and waste (approximate composition of: 35% Np-237, 27% Am-243, and 44% Cm) would be irradiated in a heavy water reactor. Approximately 500 to 1000 kg of actinides would be transmuted.

Soviet high-level wastes that are vitrified, will be stored in canisters for 30-50 years, then placed in a deep geologic repository. R&D on repositories is ongoing, and a candidate site may be named in the early 1990s. Vitrified ILW may be combined with high-level wastes and placed in a deep geologic repository. No reference disposal concept has been developed by the Soviets, but several basic concepts have been considered [KEDROVSKIY-1979, -1989, -1990].

B.14 United States (U.S.)

Nuclear Power Capacity (1990)	100 GWe
Reactor Mix	38 BWRs, 73 PWRs, 1 FBR, 1 HTGR
Reprocessing Plant Location	West Valley, NY; Savannah River, SC; Hanford, WA
Expected Glass Production	Cumulative to year 2020 [DOE-1990] - Commercial wastes (assumes no future reprocessing): 74,800 MTU spent fuel; 210 m^3 vitrified HLW. Defense wastes: 368,000 m^3 HLW (~3,500 m^3 as glass from Savannah River)

The U.S. has developed and maintains all aspects of the nuclear fuel cycle. Although U.S. policy allows for the reprocessing of commercial spent fuel, private industry has decided not to reprocess spent nuclear fuel (primarily due to economics) after the only commercial operating reprocessing plant (at West Valley, New York) shut down in 1972. Except for the small amount of commercial HLW generated at West Valley, it is planned to dispose of spent nuclear fuel directly in deep geological repositories. Extended interim storage of spent fuel and HLW awaiting disposal will be the responsibility of the federal government after its acceptance by the U.S. Department of Energy (DOE). The DOE is responsible for the planning and development of national energy strategies and implementing programs for the management of nuclear wastes from both civilian and federal activities. The DOE Office of Civilian Radioactive Waste Management (OCRWM) manages all aspects of transportation, extended interim federal storage, and disposal of civilian spent fuel and HLW and disposal of defense HLW. The DOE Office of Environmental Restoration and Waste Management (EM) manages all aspects of treatment, storage, and disposal of HLW wastes at DOE sites. The DOE Idaho Operations (ID) field office manages work by contractors of the West Valley vitrification facility and site cleanup projects.

The U.S. has carried out major R&D on reprocessing, starting with defense activities in the early 1940s. The federal R&D has developed the bismuth phosphate, REDOX, and PUREX processes to routine production scale. Federal R&D continues to support and improve the existing defense reprocessing facilities and to develop new processes, such as the TRUEX process for improved removal of actinides from wastes. Private industry also carried out significant R&D in support of their private reprocessing ventures in the 1960s and 1970s. Commercial reprocessing was conducted from 1966 to 1972 at the West Valley Plant, now being decommissioned. Construction of the Morris, Illinois, and Barnwell, South Carolina, commercial reprocessing plants was completed but the plants never operated. Reprocessing of defense fuels is carried out at Savannah River, South Carolina, and also formerly at Hanford, Washington. Reprocessing of nuclear submarine and test reactor fuels is carried out at a site near Idaho Falls, Idaho; all current reprocessing plants use the PUREX solvent extraction process. The only civilian HLW is stored at the shutdown West Valley reprocessing plant.

Acid HLW is stored in a stainless steel underground tank, and alkaline HLW is stored in a mild steel underground tank. The wastes have been kept below about 60°C by water cooling of the tanks through internal cooling coils. After vitrification in 1996-1998, the canisters of vitrified HLW will be stored onsite in an air-cooled hot cell until shipment to the geologic repository [DOE-1990]. Defense HLW is stored at Savannah River and Hanford, Washington, as alkaline wastes in large double-shell mild steel tanks in below ground concrete vaults (some older HLW at Hanford is stored in single-shell mild steel tanks), and at INEL as acid waste in double-shell stainless steel tanks. Granular HLW calcine at INEL has been stored in underground, air-cooled stainless steel bins since 1963. Capsules of solid cesium-137 chloride and strontium-90 fluoride separated from HLW at Hanford are stored in a water pool.

Glass Production

The U.S. plans to immobilize HLW from the shutdown West Valley reprocessing plant and defense-related activities by constructing and operating plants for the vitrification of HLW in the West Valley demonstration project (210 m^3 as glass) and for defense HLW in the Defense Waste Processing Facility (DWPF) at Savannah River (~3,300 m^3 as glass), the future Hanford Waste Vitrification Plant (HWVP), and a future waste processing facility at Idaho Falls. Civilian and most defense high-level liquid wastes (HLW) in the U.S. are to be converted to borosilicate glass by the liquid-fed ceramic melter process. HLW (both defense and civilian) will be converted to borosilicate glass with about 28% wastes oxides at processing temperatures of about 1150°C. The commercial HLW glass will be poured into stainless steel canisters. The canisters are 24-in. (61 cm) in diameter, 118-in. (3 m) long, and have a 0.375-in. (0.95 cm) thick wall. Each canister will hold vitrified HLW from about 2 MTU of commercial spent fuel. Defense HLW glass will be poured into stainless steel canisters that are similar to those for commercial HLW glass. Each canister will hold vitrified HLW from about 0.51 MTU of defense spent fuel. At Hanford, Washington, much of the Cs-137 and Sr-90 has been chemically separated from the HLW and converted to solid cesium chloride and strontium fluoride and placed in double-walled metal capsules for pool storage. HLW at INEL have been converted to a granular calcine, as a waste form for interim storage, in a fluidized-bed calciner since 1963. Several options are still under consideration for the final waste form for disposal, including borosilicate glass and ceramic waste forms. Conversion of the wastes to the final form will be started in the early 2000s.

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