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Final Report of the Defense High-Level Waste Leaching Mechanisms Program

August 1984

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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Final Report of the Defense High-Level Waste Leaching Mechanisms Program

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Final Report of the Defense High-Level Waste Leaching Mechanisms Program

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INTRODUCTION

The Defense High-Level Waste Leaching Mechanisms Program was a 3-year multi-laboratory cooperative research program conducted in fiscal years 1982 through 1984 and sponsored by DOE's High-Level Waste Technology Program Office at the Savannah River Laboratory.

Background

The Defense Waste Processing Facility (DWPF), the first large-scale production facility to produce nuclear waste glass in the U.S., is under construction at the Savannah River plant, and will be producing canisters of borosilicate waste glass in about 5 years. After a period of interim surface storage it is planned that the canisters of DWPF glass will go to a Federal repository for final disposal. At some later time, probably at least hundreds of years from now, it is assumed that water may contact the waste canisters.

Because contact with water offers the greatest likelihood for transport of radioactivity away from the waste form, the leaching behavior of nuclear waste glasses has been studied extensively for several years in many laboratories in the U.S. and abroad. There is informal exchange of technical information among the investigators, but until the advent of the Defense High-Level Waste Leaching Mechanisms Program (hereafter termed simply the Leaching Mechanisms Program) there had been no formal coordination of the activities of investigators in the United States. The Leaching Mechanisms Program was designed to rectify that situation and marshal the expertise at three U.S. universities, one industrial research laboratory and two DOE laboratories in a coordinated multiyear program to study the leaching behavior of defense HLW glass.

Objective

The objective of the Leaching Mechanisms Program was to determine the dominant leaching mechanisms for defense waste glass and to evaluate the effects of some major potential environmental parameters upon the leaching mechanisms.

Program Organization

The organization of The Leaching Mechanisms Program is shown in Figure 1. The participants were selected because of their experience and expertise in the field of leaching of nuclear waste forms. J. E. Mendel administered the subcontracts and coordinated the program; J. A. Stone was technical liaison for the sponsor. Several laboratory investigators, in addition to the principal investigators, contributed to the program at each participating site, except LLNL. The work at LLNL was computer code development, which did not involve laboratory experimentation.

Strong emphasis was placed on promoting coordination of the activity of the participants. Among the means used for coordination were the following:

- A standard waste form and metal container material were supplied to each participant for use in their experiments (see Appendix A for further details).

Figure 1. Organization of the Leaching Mechanism Program

- Monthly reports were exchanged among the participants.
- Periodic meetings of a Steering Committee, made up of the principal investigators, the two consultants, and sponsor representatives, were held.
- The program coordinator and technical liaison made on-site visitations at approximately 6-month intervals.
- A series of workshops, listed below, were held at which the participants presented progress reports on their work to invited outsiders including representatives of DOE and NRC staffs.
 - First Workshop, October 27-29, 1981, Seattle, Washington (PNL-4228 is a summary report of this workshop).
 - Second Workshop - May 19-21, 1982, Gaithersburg, Maryland (PNL-4382 is a summary report of this workshop).
 - Third Workshop, December 7-8, 1982, Thousand Oaks, California (PNL-4810 is a summary report of this workshop).
 - Fourth Workshop, June 20, 1983, State College, Pennsylvania.
 - Fifth Workshop, December 7-8, 1983, Oakland, California.

Summary reports will not be issued for the fourth and fifth workshops. The information presented at these workshops is adequately covered in this final report.

Format Of This Report

The report is organized into seven free-standing chapters, plus three appendices. The report is a cooperative effort, but primary responsibility for individual chapters and appendices corresponds to the major thrust of the individual participant's research activities, as follows:

Chapter or Appendix Title	Participant(s) Having Primary Responsibility
1. Mechanisms of Defense Waste Glass Corrosion: Dissolution of Glass Matrix	Catholic University of America
2. Surface Layers in Leached Borosilicate Glass High-Level Defense Nuclear Waste Forms	Rockwell Science Center
3. Environmental Interactions	University of Florida
4. Dissolution of Specific Radionuclides	Pennsylvania State University and Pacific Northwest Laboratory
5. Radiation Effects	Pacific Northwest Laboratory
6. Phenomenological Models of Nuclear Waste Glass Leaching	Catholic University of America

Chapter or Appendix Title	Participant(s) Having Primary Responsibility
7. PROTOCOL, A Numerical Simulator for Glass Dissolution	Lawrence Livermore National Laboratory
Appendix A - Reference Materials	Pacific Northwest Laboratory
Appendix B - Use of PROTOCOL	Lawrence Livermore National Laboratory
Appendix C - Leaching Mechanisms in Polyphase Ceramic High-Level Nuclear Waste Forms	Rockwell Science Center and Pennsylvania State University

Each chapter is headed by an executive summary, and has a separate table of contents and list of references. An effort has been made to minimize repetition between chapters, but some is unavoidable, given the multiple authors and the desire to have each chapter stand alone as much as possible. The authors have included many current references to other work related to the topics of their chapters, thus we believe each chapter accurately incorporates the state-of-the-art of its topic.

**SUMMARY
AND
CONCLUSIONS**

SUMMARY AND CONCLUSIONS

The Defense High-Level Waste Leaching^(a) Mechanisms Program brought six major U.S. laboratories together for three years of cooperative research. The participants reached a consensus that solubility of the leached glass species, particularly solubility in the altered surface layer, is the dominant factor controlling the leaching behavior of defense waste glass in a system in which the flow of leachant is constrained, as it will be in a deep geologic repository. Also, once the surface of waste glass is contacted by ground water, the kinetics of establishing solubility control are relatively rapid. The concentrations of leached species reach saturation, or steady-state concentrations, within a few months to a year at 70 to 90°C. Thus, reaction kinetics, which were the main subject of earlier leaching mechanisms studies, are now shown to assume much less importance.

The dominance of solubility means that the leach rate is, in fact, directly proportional to ground water flow rate. Doubling the flow rate doubles the effective leach rate. This relationship is expected to obtain in most, if not all, repository situations.

The participants in the Leaching Mechanisms Program were given specific assignments to be conducted in a cooperative manner. Executive summaries from each assignment follow.

ASSIGNMENT NO. 1: DESCRIBE THE LEACHING OF THE GLASS MATRIX AS A FUNCTION OF GLASS COMPOSITION, LEACHANT FLOW RATE, TEMPERATURE AND LEACHANT COMPOSITION.

SUMMARY: At sufficiently low flow rates the release rate of waste glass matrix components is directly proportional to flow rate (Region A in illustration below). In this region the concentration of components in the leachate is nearly independent of flow rate. In the case of some matrix components (Si, Al) this concentration is determined by saturation with respect to the surface of the glass, as modified by the leaching process and possible alteration reactions. Furthermore, the modified surface forms a barrier against migration which effectively retards the release of all glass

(a) The term leaching is used here in the same broad sense that has become conventional in nuclear waste studies, that is, the one term encompasses all of the diverse reactions that may occur when water in any form contacts waste glass.

components, including even the most soluble species (Na, B). The resulting steady-state concentrations of such species are very low compared with their solubilities.

Relatively acidic (high-silica content) waste glasses exhibit Region A behavior at higher flow rates than relatively basic (high-soda content) waste glasses because of the effect of pH on solubility. In the case of the Defense Waste Reference Glass, the pH rise is moderate and solubilities do not exhibit a very large increase even at the slowest flow rates. Furthermore, the nearer the incoming water is to saturation with respect to compounds of the waste glass matrix components (in particular silicates) the further Region A moves to the right in the illustration.

At sufficiently high flow rates, the release rate becomes constant, limited by the kinetics of the dissolution of the glass matrix (Region B in the illustration above). Increased glass surface area (e.g., due to fracture) increases the extent of release in Region B but does not affect the release in Region A. Present indications are that flow conditions permitting Region B behavior are highly unlikely in a geologic repository. The temperature dependence of the release of glass components is different in Regions A and B, with temperature effects being much larger in Region B.

ASSIGNMENT NO. 2: MEASURE THE PHYSICAL AND CHEMICAL PROPERTIES OF THE SURFACE LAYERS FORMED AS A RESULT OF LEACHING OF BOROSILICATE WASTE GLASSES TO PROVIDE MECHANISTIC INFORMATION ON THE PROCESSES INVOLVED.

SUMMARY: Dehydrated surface layers on leached glass samples were examined by electron microscopy and analytical spectroscopic techniques to observe their morphology, chemical composition, and crystallinity. Comparison of SEM/EDXS, SIMS, SIPS and XPS chemical depth profiles and physical layer thickness data with solution concentration measurements yielded good agreement, supporting the validity of observations made on dehydrated layers. Pertinent features observed in the surface layers are illustrated below:

The interface between the altered layer and the bulk glass was observed to be physically and chemically well defined, except for a narrow (<1 micron) imperfectly characterized reaction zone in the glass below the alteration layers in which depletion of only the most soluble elements (B, Li, Na, Cs) could be measured. The sharp boundary between the alteration layers and the bulk glass, the marked elemental distributions within the alteration layers, and the well-defined physical features of the alteration region indicate that its properties are directly affected by reactions with the aqueous environment and are not simply the result of incongruent dissolution of the glass matrix. Dilute leachants produce thick, low-density surface layers. Concentrated leachants characteristic of low-flow or static experiments (and silicate ground waters) produce thin, higher-density surface layers. The presence of metallic Fe in oxygenated leaching environments accelerates the dissolution process through iron-silicate reactions, producing alteration layers dominated by Fe chemistry.

Reaction products forming in and on the alteration layers in testing at 90°C and below are consistent with those found in hydrothermal leaching studies and with observations made on analogous natural geochemical systems.

ASSIGNMENT NO. 3: EVALUATE THE EFFECTS OF POTENTIAL REPOSITORY ENVIRONMENTS ON THE LEACHING OF WASTE GLASSES.

SUMMARY: Waste glass will be encased in a 304L stainless steel canister, and ground water cannot contact the glass in the geologic repository environment until the stainless steel canister fails. Tests have shown that the residual stainless steel remaining after canister failure has no effect on glass leaching. But the immediate leaching environment in the repository will also contain additional metal, probably ductile iron, in the form of overpack or borehole casing, backfill consisting of fragmented repository rock and possibly a bentonite clay, plus ground water that is at least partially in equilibrium with this system.

Laboratory and field system tests were carried out to evaluate the effect of these variables on the leaching mechanisms. In comparison to pure water, the rates of leaching for most elements are decreased in ground water and increased in the presence of bentonite and ductile iron (under oxic conditions). Ground water contains relatively large concentrations of silicon which reduces the amount of silicon that can be extracted from the glass before saturation is reached and thus reduces the driving force for glass dissolution. Iron causes the formation of colloids while bentonite provides sorption sites. Both reduce the effective concentration of glass species in solution thereby increasing their extraction from the glasses.

Field tests have been conducted in a granite bore hole several hundred meters underground in the Stripa mine in Sweden. The relative leach behavior of various waste glasses has been found to be the same in these field tests as in the laboratory tests. Sample configurations in the burial experiment provide high effective SA/V ratios which more closely approximate the physical condition of the repository than most laboratory tests. Under these conditions, waste glass leaching is low, again due to the same solubility effects observed in laboratory tests, and even the effect of bentonite seems to diminish after one year.

ASSIGNMENT NO. 4: INVESTIGATE THE DISSOLUTION OF LONG-LIVED RADIONUCLIDES FROM WASTE GLASS. BECAUSE THESE RADIONUCLIDES ARE MULTIVALENT, THE INVESTIGATION MUST INCLUDE EXAMINATION OF METHODS TO MEASURE AND CONTROL Eh OF THE LEACHING SYSTEM.

SUMMARY: The dissolution behavior of technetium, uranium, neptunium and plutonium from defense waste reference glass was studied. The effect of Eh on the leaching behavior of technetium and uranium was found to be significant because the valence states have different solubilities: e.g., U^{6+} (soluble)/ U^{4+} (insoluble) and Tc^{7+} (soluble)/ Tc^{4+} (nearly insoluble). Special precautions were taken to incorporate technetium in the waste glass as Tc^{4+} in order to obtain a homogeneous distribution of technetium in the glass matrix.

A properly-cleaned platinum electrode was found satisfactory for measuring Eh. Equilibrium redox conditions were found to pertain only at the extreme upper and lower ends of the Eh range, that is, near the upper and lower stability limits of water. Experimentally, the former was obtained by contact with air, the latter by continuous bubbling of forming gas through the leaching system in the presence of a palladium catalyst.

The dissolution of Tc from the waste glass under oxidizing conditions followed a mixed linear-parabolic kinetics and was strongly influenced by the initial pH of the solution. Dissolution of Tc was slowed by several orders of magnitude under highly reducing conditions. Uranium dissolved incongruently under oxidizing conditions but with the same time dependence as the glass-forming elements. The ratio of U/B in the leachate varied with pH. The ratio was lowest in the near-neutral pH regimes.

The dissolution behavior of neptunium and plutonium was studied only at high Eh, which should yield the most soluble species. The form of the transuranics leached from waste glass was found to be at least partially associated with colloidal-sized particles (held on a $1.8 \mu m$ filter) in almost all tests. With deionized water leachant, the leached transuranics were almost totally filtered out; but with brine leachants the transuranics passed through the filter, showing that soluble species were dominant. Simulated ground water leachants tended to exhibit an intermediate behavior. Leached uranium exhibited a much smaller tendency to be associated with colloidal species than did neptunium and plutonium.

ASSIGNMENT NO. 5: INVESTIGATE THE EFFECTS OF RADIATION ON LEACHING MECHANISMS.

SUMMARY: The principal radiation effects of concern are: a) radiation-induced changes in the waste glass, b) radiolysis at the glass: water interface, and c) radiation-induced changes in the repository environment, including effects on the host rock that may alter water chemistry. Measurable density change in waste glass begins at a cumulative dose of about 1×10^{23} alpha decays/ m^3 and saturation at a dose of approximately 5×10^{24} alpha decays/ m^3 . Leach rates increase by less than a factor of three even in waste glass with a saturated radiation dose. Radiolysis of repository fluids can yield a complex spectrum of products, including, in addition to the normal radiolytic products of water, oxalic and nitric acids from radiolysis of CO_2 and dissolved N_2 , oxidizing chlorine species from radiolysis of Cl^- , and high molecular weight organic

compounds from radiolysis of methane. These effects may be mitigated by the presence of host rock and engineered barrier materials, as well as additional redox-sensitive, dissolved species. Tests designed to isolate the effects of the radiolytic products of water on the leaching of plutonium from defense waste glass were performed as part of the Leaching Mechanisms Program. The radiolytic products enhanced the leach rate by about a factor of two.

ASSIGNMENT NO. 6: DESCRIBE THE STATUS OF MATHEMATICAL MODELING OF THE LEACHING MECHANISMS FOR NUCLEAR WASTE GLASS.

SUMMARY: Data developed in the Leaching Mechanisms Program, and elsewhere, show that continued leaching of waste glass at almost any given set of conditions leads ultimately to steady-state (or quasi-steady-state) concentrations of all leached species. The mathematical models being developed to predict leachant concentration as a function of time depend in varying degrees upon knowing empirically-derived dissolution rate constants, effective diffusion coefficients in the bulk glass and in "protective layers", saturation concentrations for the glass constituents, and the identity of alteration products that form on the glass surface.

Most modeling emphasis has been placed on kinetic behavior during short-term leaching (<1 year), and the fitting of experimental data in this time regime has been achieved successfully in several limited instances. However, no general application of any of the models has as yet been achieved, especially as regards the long-term leaching (hundreds or thousands of years) that is of interest in the context of a geologic repository. Here some models predict (in the absence of waste form-leachant interactions) a $t^{1/2}$ dependence for the leachant concentration growth, others imply a t^1 dependence. Of course, under leachant saturation conditions that will likely obtain in the repository environment, t^0 behavior must be expected.

As part of the Leaching Mechanisms Program, workers at Catholic University have begun development of a phenomenological model that yields a smooth transition in the evolution of the concentration of various species in the leachant from a kinetically-controlled t^1 initial growth to long-term steady-state t^0 behavior. The mathematical structure in which the model is phrased naturally accounts for the transient peaking in the leachant concentrations under slow-flow conditions, and also allows for specifying the static long-term behavior of soluble glass components in terms of a leach-inhibiting protective barrier resulting from saturation with respect to high silica content alteration products formed at the glass surface.

ASSIGNMENT NO. 7: DEVELOP THE COMPUTER CODE PROTOCOL AND ITS APPLICATION TO THE SIMULATION OF THE DISSOLUTION REACTIONS OF NUCLEAR WASTE GLASSES BY GROUND WATERS.

SUMMARY: A FORTRAN version of PROTOCOL, including subroutines for online graphics, is set up on the CRAY-1 at Lawrence Livermore National Laboratory, and can be accessed through arrangements with the U.S. DOE. The code contains 1) a kinetic capability to describe release from the glass, 2) an equilibrium capability based on the geochemical code MINEQL that models solution concentrations and precipitate formation, 3) a system-monitoring capability that directs the computations

through a series of discrete time increments, and 4) a capability to estimate the standard Gibbs free energy function of poorly characterized solid phases.

Within the constraints of available data, PROTOCOL has achieved its intended purpose. It has been developed into a flexible instrument for the evaluation of both experimental and theoretical approaches to the dissolution of solids. Conventional solubility considerations are also extended to non-stoichiometric alteration products of glasses. Many of the precipitates that form in leaching of waste glass are as yet unidentified, hydrous, poorly-ordered species that cannot be accommodated by the standard thermodynamics-based geochemical code. PROTOCOL contains a subroutine based on modifications of Y. Tardy and R. M. Garrels ("A Method of Estimating the Gibbs Energies of Formation of Layer Silicates," *Geochim et Cosmochim Acta*, 38:1106-1116, 1974) that shows promise of identifying thermodynamic "building blocks" from which the hydrous precipitates in the leached surface layer may be assumed to be composed in varying combinations.

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A large number of people, more than I can possibly name here, have made it a pleasure to be associated with the Leaching Mechanisms Program. First and foremost, thanks to the principal investigators for their willingness to work together and make this a truly cooperative effort. We are all grateful to the sponsors at SRL for their vision in setting up a 3-year program and for the consistency of their support throughout the program, first from Phil Permar, Tom Bernadzikowski and Don Gordon, and then from Pete Gray and Ed Hennelly. Bruce Wilson, DOE-SR, took an active and much-appreciated interest in the program, as did Ray Walton, DOE-HQ. Don Runnells, John Kircher and, early on, Gil Raines, made valuable contributions to our Steering Committee. Special thanks to Diane Knight, who helped Will White host our workshop at Penn State, and to Alan Harker and Don Jackson, who hosted our workshops at Thousand Oaks and Oakland, respectively. Thanks also to George Barton who helped Don Jackson set up for the PROTOCOL open house at LLNL. Billie Neth has been invaluable as arrangements and recording secretary throughout the program. Judy Hooper, Pam Whiting and Jim Thielman have ably edited this and previous reports from the program. And finally, I have enjoyed the association with John Stone. I believe our onsite visits to the participants contributed greatly to the success of the program.

John Mendel
Coordinator, Leaching Mechanisms Program

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John Bunnell
Coordinator, Teaching Achievement Program

CHAPTER 1

MECHANISMS OF DEFENSE WASTE GLASS CORROSION: DISSOLUTION OF GLASS MATRIX

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CHAPTER 1

Mechanisms of Defense Waste Glass Corrosion: Dissolution of Glass Matrix

ASSIGNMENT: DESCRIBE THE LEACHING OF THE GLASS MATRIX AS A FUNCTION OF GLASS COMPOSITION, LEACHANT FLOW RATE, TEMPERATURE AND LEACHATE COMPOSITION.

SUMMARY: At sufficiently low flow rates the release rate of waste glass matrix components is directly proportional to flow rate (Region A in illustration below). In this region the concentration of components in the leachate is nearly independent of flow rate. In the case of some matrix components (Si, Al) this concentration is determined by saturation with respect to the surface of the glass, as modified by the leaching process and possible alteration reactions. Furthermore, the modified surface forms a barrier against migration which effectively retards the release of all glass components, including even the most soluble species (Na, B). The resulting steady-state concentrations of such species are very low compared with their solubilities.

Relatively acidic (high-silica content) waste glasses exhibit Region A behavior at higher flow rates than relatively basic (high-soda content) waste glasses because of the effect of pH on solubility. In the case of the Defense Waste Reference Glass, the pH rise is moderate and solubilities do not exhibit a very large increase even at the slowest flow rates. Furthermore, the nearer the incoming water is to saturation with respect to compounds of the waste glass matrix components (in particular silicates) the further Region A moves to the right in the illustration.

At sufficiently high flow rates, the release rate becomes constant, limited by the kinetics of the dissolution of the glass matrix (Region B in the illustration above). Increased glass surface area (e.g., due to fracture) increases the extent of release in Region B but does not affect the release in Region A. Present indications are that flow conditions permitting Region B behavior are highly unlikely in a geologic repository. The temperature dependence of the release of glass components is different in Regions A and B, with temperature effects being much larger in Region B.

CHAPTER 1

Mechanisms of Delicate Waste Gas Condensate: Dissolution of Glass Matrix

ASSIGNMENT: DESCRIBE THE BEHAVIOR OF THE GLASS MATRIX AS A FUNCTION OF GLASS COMPOSITION, REACTANT FLOW RATE, TEMPERATURE AND LIQUID COMPOSITION.

SUMMARY: An illustration for how the release rate of waste gas matrix can be directly proportional to flow rate (Region A) in a situation below is the region of concentration of concentration is the release is nearly independent of flow rate. In the case of some matrix components (e.g. the concentration of dissolved gas) the release rate is proportional to the square of the flow rate (Region B) and possible slight variations in the release rate of the matrix components (e.g. the release rate of the matrix components) is proportional to the square of the flow rate (Region C). The resulting steady-state concentration of each species is very low compared with their solubility.

Relatively early this - little control was shown for Region A behavior. In this flow rate (Region A) the release rate is nearly independent of the effect of flow rate. In the case of the delicate waste gas matrix (e.g. the release rate of the matrix components) the release rate is nearly independent of flow rate. Furthermore, the release rate of the matrix components is proportional to the square of the flow rate (Region B) and possible slight variations in the release rate of the matrix components (e.g. the release rate of the matrix components) is proportional to the square of the flow rate (Region C).

At relatively high flow rates, the release rate becomes constant, limited by the kinetics of the dissolution of the glass matrix (Region A) in the situation above. In the case of some matrix components (e.g. the concentration of dissolved gas) the release rate is proportional to the square of the flow rate (Region B) and possible slight variations in the release rate of the matrix components (e.g. the release rate of the matrix components) is proportional to the square of the flow rate (Region C). The resulting steady-state concentration of each species is very low compared with their solubility.

DISSOLUTION OF GLASS MATRIX

1.1 OVERVIEW

SYNOPSIS

The mechanisms which control glass corrosion depend on the composition of the glass, on its environment (e.g., on the initial composition of the aqueous medium and the temperature), and on time. Two types of time dependence have to be considered. These involve the total exposure time and the contact time, respectively, with a particular volume of leachant. The total exposure time of the glass controls the transformation of its surface from its dry original state to a form which is in steady state with respect to interaction with the aqueous environment. During this time the corrosion rates change, reflecting for instance the build-up of a hydrated layer. This is a transient effect, and in the long term the rate of material loss is likely to become constant. The value of this rate will depend on the contact time between the glass and the solution. This contact time (which is inversely proportional to the water flow rate), together with the ratio between the surface area of the glass and the volume of solution in contact with it, determines the extent to which the composition and reactivity of the solution are affected by the dissolution of the glass components, (e.g., the extent of pH rise due to alkali extraction and the extent of approach to saturation with respect to Si, Al, etc.). The long-term material loss rates are likely to be determined by the rate of network dissolution (at high flow rates) or by saturation of the aqueous medium with respect to components of the glass or of its crystalline alteration products (at slow flow rates).

The mechanism and rates of the corrosion processes which take place when a glass is exposed in an aqueous environment are determined by a combination of physical parameters, such as temperature, and chemical factors, viz. the compositions of the glass and of the aqueous medium in contact with it. These two chemical factors can control the

glass corrosion process independently or in combination, depending on the extent to which the aqueous medium is affected by the accumulation of glass dissolution products. The extent of interaction is determined in its turn by the rate at which the water in contact with the glass is replaced and by the ratio between exposed surface of glass and the volume of water in contact with it. (As will be shown later, in many cases the flow rate and the dilution factors can be treated together in terms of a single parameter corresponding to contact time under standard dilution conditions.)

The strong dependence of the corrosion behavior of glasses on the extent of interaction with the leachant and on the resulting changes in leachant chemistry can be illustrated by first considering two extreme cases. The first one occurs under conditions of high dilution, but similar behavior results when glass is exposed to rapidly flowing water. More generally, this is the constant-medium or noninteractive case. In this case the accumulation in the leachant of species leached out of glass is too small to alter the composition of the leachant in a sufficient measure to affect its reactivity toward the glass. In particular, the pH of the aqueous medium remains at the same level as before contact with the glass, and the concentrations of solubility-limiting components, such as Si and Al, in the aqueous medium, relative to their saturation limits, do not significantly change as a result of contact with the glass. In this case the rate law and the leach rate of a particular glass depend only on the original leachant composition.

The second limiting case is that of a large glass surface exposed to water for prolonged periods under stagnant conditions. This is the fully interactive case where the composition of the aqueous medium is strongly coupled with that of the glass. The final pH is primarily determined by the leaching of alkalis and acidic components (such as the buffering, weakly acidic silicon and boron

oxides) out of the glass, and saturation of major glass components such as Si and Al is of primary importance in determining their levels in the aqueous phase.

The most likely scenario for the transport of hazardous components out of a nuclear waste form involves flow of water through a geologic repository. Depending on the rate of water flow, glass corrosion processes may exhibit noninteractive behavior (at high flow rates) or strongly interactive behavior (at low flow rates). At intermediate flow rates glass corrosion undergoes a transition from one type of behavior to the other. However, the range of flow rates at which this transition occurs varies from one glass to another. In the case of low-alkali, high-silica glasses, for instance, both alkali leaching and matrix dissolution are slow and effects of product accumulation (pH rise, saturation) are observed only at very slow flow rates. The reverse is true in the case of high-alkali glasses. The leachant composition and temperature are also important. For instance, in ground waters containing high concentrations of silica the onset of saturation effects appears at higher flow rates than in deionized water.

The modification of the composition and structure of the surface regions of multicomponent glasses after leaching is primarily due to differences in solubility among their various components. Those components which form soluble oxides, such as the alkalis, the heavier alkaline earths (such as Ba), B, Mo and, in some cases, P, leach out first and are replaced to some extent by water radicals (H_2O , H^+ , H_2O^+ , $-OH$, etc.). Species which are insoluble in the pH range involved, such as Fe, Ni, Mn, Mg and the rare earths in weakly basic environments, remain in the surface layers or reprecipitate or resorb on the surface as the glass matrix dissolves. The most important source of variations in the surface structure of a glass exposed to various aqueous media is the behavior of major matrix elements, especially Si and Al, which are soluble to a limited extent and their solubility is highly dependent on pH. Under conditions of near-saturation these elements tend to stay behind and form a dense, stable layer which can serve as a protective barrier for the remaining glass. Under conditions which promote rapid dissolution of these elements, i.e., low concentrations in the aqueous phase, they leach out almost as quickly as the alkalis themselves, leaving behind a loose, fragile, less protective surface layer. Rapid dissolution of the major matrix elements (Si and Al) is promoted in high-pH environments. However, due in

part to the relatively high stability of various silicates and aluminosilicates under moderately high pH conditions protective layers can apparently still form under such conditions up to pH values of approximately 12.

The surface structure is generally the key factor in determining the leach rates (Yastrebova 1961; Hensch 1977). For instance, in strongly alkaline solutions Si is highly soluble. Under these conditions the surface layers formed on simple silicate glasses are thin and unstable and the corrosion rates of the glass as a whole are very high. On the other hand, the addition to the glass of ingredients such as ZrO_2 or $Ca_2(PO_4)_3$, which have low solubility in alkaline media, causes the formation of a denser and more stable surface layer and a corresponding increase in leach resistance.

Since the surface structure is a key factor in leach kinetics, it can account for changes in leach rates when the contact time between the glass and leachant is varied. At long contact times (i.e., slow flow conditions) and high ratios of glass surface to leachant volume, the composition of the aqueous phase changes substantially as it becomes enriched both in alkalis (pH rise) and in matrix elements (Si, Al). The latter effect tends to raise the levels of the matrix elements towards their saturation limits and thus promotes their accumulation in the surface layer, rendering it denser and more protective and giving rise to smaller leach rates than those observed under rapid-flow, high-dilution conditions. This effect, however, may be reduced and even counter-balanced by the pH rise, which causes steep increases in the saturation levels of Si and Al. The extent of the pH rise at a given contact time depends on the composition of the glass, or more accurately on the ratio of basic components (e.g., alkali oxides) to acidic components (e.g., SiO_2 , B_2O_3) in the glass. Accordingly, the contact time corresponding to the transition between the two types of leach behavior as well as the extent of the transition depend on the composition of the glass, and especially on the relative concentrations of alkalis and of matrix elements, respectively.

Another important effect of contact time on surface structure, and hence on leach rates is related to stabilization and densification of the leached surface layer through the formation of a crystalline compound or compounds. Studies carried out using sealed capsules have shown this process to be quite rapid at temperatures above 150-200°C (hydrothermal conditions). At low temperatures (40-90°C)

this process may require a much longer contact time. A long contact period is necessary because the solute concentration has to reach sufficiently high levels to exceed the solubility of the more ordered, often crystalline, alteration products. Subsequently the solution must then remain in contact with the surface for a sufficiently long time for the alteration process to take place. The flow rate region at which the transition between noninteractive (or unsaturated) and strongly interactive (saturated) leach behavior occurs is therefore dependent on temperature as well as on glass composition.

The rates of glass dissolution depend on total exposure time as well as on the contact time with a particular volume of leachant. Both at high flow rates and at low flow rates the leach rates of an initially dry, fresh surface change as it becomes modified due to the action of water. The changes reflect in part physical characteristics of the initial surface finish, such as the dissolution and elimination of protuberances and adhering fines and the smoothing of rough or cracked areas (Sanders and Hench 1973). Another, more important, cause of the initial changes in leach rates is the build-up of surface layers that results from the rapid extraction of soluble glass components (alkalis, boron) and the penetration of water radicals. Both the composition of the leached layer and the duration of the build-up process depend on the chemistry of the glass and of the aqueous medium.

In analyzing the kinetics of glass dissolution it is important to take into account the configuration of the leaching system. The case of an infinite leachant volume (or its equivalent, a very rapid leachant replenishment) is relatively simple, since the build-up of solute concentrations does not have to be taken into account. At increasingly smaller leachant volumes (or slower replenishment rates) the kinetic patterns become more complicated due to increasing solute concentrations in the aqueous phase and decreasing concentration gradients between the glass and the solution. Eventually, back-reactions and saturation effects become important. The simple case of very high dilution or very rapid flow will be discussed first.

For species which exhibit selective leaching, in particular alkalis, the amount leached Q per unit area is initially proportional to the square root of time (Keppeler and Thomas 1933; Lyle 1943), i.e.,

$$Q = at^{1/2} \quad (1.1)$$

This expression reflects alkali migration through a growing layer. The coefficient a is not related, however, to the alkali diffusion coefficient in the solid glass (Rana and Douglas 1961; Kuhn and Peters 1982). Since the dissolution of alkali leads to the release of an equivalent amount of hydroxide ion which attacks and dissolves the silica network of the glass (Charles 1958), the dissolution of silica also follows in part a parabolic term (Isard, Allnatt and Melling 1982). However, another part of the expression which describes the attack of water on glass represents dissolution of the glass matrix in water, which is linear with time (Rana and Douglas 1961; Douglas and El-Shamy 1967). Accordingly, the full expression is (Holland 1966):

$$Q = at^{1/2} + bt \quad (1.2)$$

While the parabolic term dominates at short times, the linear term usually becomes rate-determining in the case of multicomponent silicate glasses, even at low temperatures, in the course of relatively short periods of time (Rana and Douglas 1961; Isard, Allnatt and Melling 1982; Douglas and El-Shamy 1967). This is particularly true in the case of nuclear waste borosilicate glasses (Kuhn and Peters 1982; Lanza and Parnisari 1979). Based on short-term experiments, values of the coefficient a for such glasses are typically between 0.1 and $0.5 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ at 90°C (Soper et al. 1983); on the other hand, minimum values of the coefficient b derived from long-term experiments on very durable glasses such as tektites are about $8 \times 10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ at 90°C (Barkatt et al. 1984a). It can be concluded that in 10 years, at most, the leach kinetics of multicomponent silicate glasses are likely to become dominated by the linear term. In short-term applications such as the corrosion of optical glass the initial parabolic time-dependence of the leaching process of the original surface is important. However, in nuclear waste glass studies the most important factor is the long-term behavior and in most cases it should be sufficient to consider the linear term bt for predictions of long-term durability in geologic disposal service. Even if available test data do not cover a sufficiently long period to eliminate the contribution of the parabolic term, this will only result in a high value in estimating the ultimate leach rate b , which will be compatible with the evaluation of conservative upper limits of the long-term extent of corrosion.

If the growing surface layer is stable, the parabolic term may take a long time to vanish, but the leach rate will eventually approach a finite nonzero value of the coefficient b corresponding to the rate of matrix dissolution. However, in many cases leached layers on complex glasses, in particular on borosilicate waste glasses, are highly unstable and undergo frequent cracking or separation. In such cases the effectiveness of the layer in limiting the attack on the glass is much smaller and a constant leach rate mechanism takes over much earlier. Another extreme case is that of glasses, where the entire alkali content of the high-alkali glass may be leached out rapidly leaving behind a silica network which is only subject to direct matrix dissolution (Douglas and El-Shamy 1967).

The above discussion was limited to the case of rapid flow/high dilution; effects of increasing solute concentration in the aqueous phase were not considered. The kinetics of glass dissolution become more complicated when the leaching process is carried out under conditions of increasingly small ratio between glass surface area and leachant volume or of increasingly low leachant replacement rates. Under these conditions, the leaching kinetics exhibit increasingly large deviations from the simple expressions (1.1) and (1.2) (Harvey, Litke and Boase 1984) due to the accumulation of dissolved glass components in the aqueous phase and a resulting decrease in the concentration gradients between the glass and the solution. The smaller concentration gradients reduce the driving force for diffusion-controlled leaching. Moreover, the net matrix dissolution process, which controls long-term behavior, can no longer be represented by the second term in eq. (1.2). The concentrations of major matrix elements (Si, Al) can now approach saturation, and the effective rate of matrix dissolution slows down. In addition, the surface layers obtained at long times now become progressively richer with respect to these elements and less porous and more likely to affect the rates of migration of material across these layers.

In the limiting case of strong interaction (long contact times) a freshly exposed glass surface is again likely to exhibit time-dependent leach rates during the early stages of the exposure. As mentioned above, a modified surface layer is likely to develop, but its composition may be quite different from the one formed at high dilution, as it reflects steady state with respect to a saturated solution and the possible formation of alteration products. The alteration process

takes place only at long contact times because it requires high solute concentrations (exceeding the solubility of the altered phase) to be present in the solution; alteration rates may be expected to be higher at slower flow rates because of the larger extent of supersaturation with respect to the altered phase. As shown below, characteristic alteration times for the surfaces of certain nuclear waste glasses at slow flow rates and temperatures of 70 to 90°C are in the range of several months to years.

As in the case of leaching at high dilution, kinetic transients in the case of low dilution are likely to vanish after a certain period. However, in the latter case the interaction at long times is characterized by a constant leachate composition, controlled by the solubilities of the principal matrix elements, rather than by a constant leach rate. Slow corrosion processes involving reprecipitation of dissolved glass components in more stable crystalline forms are likely to be linear with time since the composition of both aqueous and solid phases remain at steady state. At very slow flow rates the release of material from the waste form is likely to be controlled by the rate at which solution saturated with respect to crystalline alteration products of the glass (at solubility levels which may be much lower than those of the glass itself) migrates out of the volume in contact with the waste form and is replaced by inflowing water.

It can be concluded that the rate of mass loss from a glass which is in contact with an aqueous environment is highly dependent on time. This dependence, however, is of two completely distinct types: (1) dependence of the dissolution rate on total exposure time. This dependence follows the modification of the surface of the glass from its initial dry state to a composition which has reached steady state with respect to interaction with the solution; (2) dependence of the rate of material loss on the contact time, i.e., on the rate at which the volume of solution in contact with the glass is replaced by fresh leachant. This contact time has a major influence on the composition of the solution, and hence on its reactivity towards the glass. In the long term, the dependence on total exposure time disappears and the rate of material loss becomes a constant, which is determined by the dissolution rate of the hydrated surface and by the flow rate of the water. However, the transient dependence on total exposure time can have marked effects on the results of short-term laboratory tests, and this has to be taken into account in the design of test methods as well as in

the application of existing laboratory data for long-term extrapolation.

In summary, preliminary considerations indicate that at the long periods of time of significance in the corrosion of nuclear waste glasses the controlling features are likely to be a constant leach rate if the rates of leachant exchange are high (short contact times), and a constant leachate composition if these rates are low (long contact times). A quantitative examination of these predictions in view of experimental findings is presented below, centered on defense waste borosilicate glasses, in particular Savannah River Laboratory TDS-131 glass and the MCC Defense Waste Reference Glass.

1.2 LEACH TESTS FOR LONG-TERM DURABILITY PREDICTIONS: SERVICE CONDITIONS AND PARAMETERS

SYNOPSIS

Defense waste streams, which will have some variations in composition, will be immobilized in borosilicate glass. An approximate composition of an average defense waste glass system is the DWRG (Defense Waste Reference Glass) formulation. This formulation includes about 50% SiO_2 , 10% Fe_2O_3 , 8% Na_2O , 7% B_2O_3 , 6% Al_2O_3 and 4% Li_2O as major components. The service conditions to which these glasses will be exposed in repositories are likely to be characterized by a ground water pH between 6 and 10, temperatures of 40 to 90°C, water flow rates between 4×10^{-8} and 4×10^{-4} m/yr, and effective surface-to-volume ratios of about $1 \times 10^2 \text{ m}^{-1}$.

1.2.1 General

Since the operative leaching mechanisms and the corrosion rates of glass are highly dependent on service conditions, it is necessary to define a range of testing conditions which are suitable to the understanding of repository-relevant leach mechanisms and the evaluation of long-term leach rates. These ranges of testing parameters are listed below.

1.2.2 Glass Composition

The principal objective of the experimental program was to characterize the leach behavior of defense waste borosilicate glass compositions. The preferred representative of these glasses is the Materials Characterization Center (MCC) Defense Waste Reference Glass (DWRG). However, the leach behavior of other borosilicate glasses, in particular

Savannah River Laboratory (SRL) TDS-131, must also be considered, firstly because of the short time which has been available for experimentation on DWRG, and secondly because comparison among various borosilicate glasses has very important mechanistic implications (see Section 1.4). For the latter reason, several other borosilicate glasses are also mentioned below. The compositions of all the glasses included in the present study were determined at The Catholic University of America (CUA). These compositions are listed in Table 1.1. Two columns appear in this table for DWRG and TDS-131 glasses. The column on the left represents the analytical results obtained at CUA and the column on the right gives the composition supplied by the originating laboratory (MCC or SRL, respectively). Discrepancies with respect to major glass components did not exceed $\pm 5\%$ on a relative basis.

1.2.3 Leachants, Waste Package Materials, Temperatures, Flow Rates and Glass: Water Ratios

Expected conditions in the repository environment and the corresponding ranges of test parameters which are most relevant to the actual service conditions are described in detail in Chapter 3. Briefly, in repositories defense waste glasses will be exposed to ground water compositions initially having a near-neutral or moderately basic pH (between 6 and 10). In hard rock repositories relatively high silica levels (between 10 and 60 mg/L) are common in ground water. Both pH and silica levels are likely to change upon prolonged contact with the glass (see 1.2.4). Eh values may cover a broad range depending on the compositions of the ground water and of the waste package and on radiolysis effects (cf. Chapters 3, 4 and 5). Some of the materials which may be present in the immobilization system (which includes canister, overpack, backfill and host rock) can have significant effects on the leaching process. These materials include metals as well as oxides, silicates and aluminosilicates. Representative ground water compositions and waste package materials are included in the present study. The temperature range studied was 40 to 90°C. The value of 90°C approximates the peak temperature that may be reached (depending on the geology and packaging) in a repository during the thermal period. During this period breaching of the containment is highly unlikely. The value of 40°C represents the post-thermal ambient temperature of the waste glass forms during long-term storage. Effective surface-to-volume (S/V) ratios of about $1 \times 10^2 \text{ m}^{-1}$ are expected (allowing for fracture), and water flow rates

TABLE 1.1. Composition of Nuclear Waste Borosilicate Glasses

	DWRG		SRL TDS-131		PNL 76-68	PGM	CUBS
SiO ₂	51.6	49.0	43.9	44.1	40.0	57.3	56.9
Fe ₂ O ₃	10.1	10.05	13.6	14.4	11.1	14.8	12.9
Na ₂ O	7.7	9.20	12.1	13.7	12.9	2.7	5.4
B ₂ O ₃	7.3	6.77	9.9	10.4	9.5	3.7	4.9
Al ₂ O ₃	5.5	6.58	3.7	3.4	0.02	8.1	6.2
Li ₂ O	4.1	4.85	3.7	4.0			1.7
MnO ₂	3.4	3.09	4.5	4.1		4.0	3.9
U ₃ O ₈	2.8	2.61				1.8	1.4
NiO	2.1	2.01	2.3	1.7	0.6	2.4	1.2
CaO	1.9	1.95	0.8	1.2	2.0	0.12	0.2
ZrO ₂	1.0	0.94	0.3	0.4	1.9		0.4
MgO	0.8	0.74	1.4	1.4			0.4
SrO	0.5	0.46	0.9 ^(a)		0.4	0.11	0.4
Cs ₂ O	0.4	0.31	0.7 ^(a)		1.1	0.10	0.7
Cr ₂ O ₃	0.3	0.06			0.4		
P ₂ O ₅	0.2				0.5	4.4	3.3
TiO ₂	0.1	0.11	0.8	0.7	3.0		0.1
CeO ₂	0.04		1.0 ^(a)		3.9	0.24	
K ₂ O	0.04				0.1		
Nd ₂ O ₃	0.03				1.4	0.23	
ZnO	0.02	0.01			5.0		
CuO	0.01	0.02					
CoO	0.01				0.1		
La ₂ O ₃			0.3	0.4	1.9		
SO ₃			0.1	0.1			
MoO ₃					2.4		
BaO					0.6		
Pr ₆ O ₁₁					0.4		
TeO ₂					0.3		
Sm ₂ O ₃					0.2		
Gd ₂ O ₃					0.2		
Eu ₂ O ₃					0.1		
Y ₂ O ₃					0.02		
	99.95	98.76	100.0	100.0	100.04	100.0	100.0

(a) SRL TDS-131 was doped with Ce, Sr and Cs.

may range between 4×10^{-8} and 4×10^1 m/yr, but mass diffusion of water may raise the lower limit of the effective flow rate significantly (see Chapter 6). Flow rates used in the present study at pertinent S/V values range between 3×10^{-2} m/yr and the very high rates which might be encountered in a worst accident scenario.

1.2.4 pH Effects on Glass Dissolution

The parameters considered in the previous sections (i.e., the compositions of the glass, the leachants and other waste package components, the flow rate of the leachant, the surface-to-volume ratios and the temperature) establish the range of pH values which

may be expected under breached repository conditions. The pH has a major influence on the rates and mechanisms of silica-based glass dissolution (Morey 1954). This is also true in the case of crystalline silicates, which are often characterized by a rate equation with a forward term proportional to $(a_{H^+})^n$, where (a_{H^+}) is the activity of the protons and n is typically 1 in the acid region and between -0.2 and -0.5 in the alkaline region, indicating that in basic environments hydroxide ions promote silicate dissolution (cf. Chapter 4).

In the case of glasses, the acceleration of the dissolution process when the pH increases can be directly related to the simple mechanism proposed by Charles (1958) for an alkali-containing silicate glass:

This mechanism accounts for both the observation that upon leaching silicate glasses in more basic leachants the rates of glass dissolution sharply rise, and the fact that upon prolonged contact of glass with initially neutral water the pH rises and the major mechanism of attack on the glass changes from diffusion-controlled alkali extraction to direct matrix dissolution (Rana and Douglas 1961). Alkali accumulation and pH rise account for the earlier onset of matrix dissolution at high S/V ratios (Ethridge, Clark and Hensch 1978; Van Iseghem, Timmermans and de Batist 1984).

At long contact times the loss of material from the glass becomes controlled by solubility (cf. Section 1.4). The solubility of silica, which is the major matrix building-block of the glass, at a given temperature is determined by the pH due to the conversion of scarcely soluble neutral silica to highly soluble silicate ions at increasing hydroxide ion concentrations. The solubility, S_t , can be expressed (Alexander, Heston and Iler 1954) as

$$S_t = S_m(1 + 10^{\text{pH}-\text{pK}}) \quad (1.6)$$

where S_m is the solubility in neutral or acidic media and pK is the dissociation constant of silicic acid, which is 9.75 ± 0.15 between 20 and 35°C and 9.2 ± 0.1 between 60 and 100°C (Baes and Mesmer 1976). In highly basic media S_t is simply proportional to $[\text{OH}^-]$. Similar expressions can be applied to the increase in solubility of other important

glass components, such as alumina, when the pH becomes increasingly alkaline (Dezelic, Bilinski and Wolf 1971). In the case of alumina, the pK value corresponding to the formation of aluminate is approximately 7.7 (Baes and Mesmer 1976) and similar or lower values apply in the cases of complex aluminosilicates (Tole 1982; Barkatt et al. 1982).

In the specific case of defense nuclear waste glass it was shown (Plodinec, Wicks and Bibler 1982; Wicks et al. 1982) that the leach rates sharply and exponentially increase when the pH rises above a critical value of approximately 9.5, which corresponds to the onset of rapid network dissolution due to nucleophilic attack of the hydroxide ion on the silicon-oxygen matrix (Budd 1961). Glasses of this type, which contain a relatively large amount of alumina are also subject to rapid attack in acid environments ($\text{pH} < 4.5$). The commercial waste glass PNL 76-68 (Mendel et al. 1977), which contains very little alumina (cf. Table 1.1) exhibits a much smaller rise in leach rates in increasingly alkaline or acidic media (Ross et al. 1978; Barkatt, Barkatt and Sousanpour 1982) compared with defense waste glasses (Plodinec, Wicks and Bibler 1982). Acidic pH values can result from radiolysis of water containing nitrogen or CO_2 (Barkatt, Barkatt and Sousanpour 1982). However, under repository conditions the pH is likely to be above 7 due to combination of the alkalinity of ground water (except in the case of salt brine) and the extraction of alkali from the glass (Plodinec, Wicks and Bibler 1982). The latter effect is highly dependent on glass composition, as detailed in Section 1.4 below. The degree to which it can increase the pH of the water depends on the effective contact time between glass and water, i.e., on the flow rate and S/V ratio. Higher temperatures result both in more rapid alkali extraction and accumulation and in narrowing of the region of slow, initially electrophilic attack on the glass, i.e., rapid network dissolution becomes predominant at approximately pH 8.5 to 9 at 90°C instead of approximately 9.5 at 25°C (Wicks et al. 1982).

As a result, the pH of the solution in contact with the glass may be expected to lie between 8 and 9 in a repository which contains waste glass of low alkali content or is subject to rapid water flow and very high values in the case of a repository which contains a highly alkaline waste glass under slow water flow conditions. Alkali extraction from certain waste glasses was indeed observed to raise the leachate pH up to 12.4 in the case of SRL TDS-131 glass (see Section 1.4) and 13.1 in the case of certain

European glasses leached at high temperatures (Van Iseghem, Timmermans and de Batist 1984). The presence of ductile iron in the waste package tends to raise pH values (McVay 1982) (cf. 1.5.6). Based on the discussion above, it can be concluded that if the glass/waste package design results in a pH range of approximately 6.5 to 9.5, the performance of the system can be optimized. Conversely it is very important to carry out leach tests that can predict long-term maximum values of the pH of the system. The extent of the effect of glass leaching on the pH at a certain distance from the glass surface depends on the repository configuration. For instance, in a repository which does not contain a backfill this effect is likely to be significant over larger distances than in a repository filled with crushed rock. In any case, the pH in the interaction zone between the glass and the solution, which is likely to consist of voids and cracks inside a breached canister, can be expected to be determined by the waste form with possible contributions from the canister and overpack materials.

1.3 LEACH TESTS FOR LONG-TERM DURABILITY PREDICTIONS: TEST METHODS AND APPLICABILITY FOR MECHANISTIC STUDIES

SYNOPSIS

Test methods useful in establishing long-term trends and mechanisms of glass durability have to fulfill several criteria. These include elimination of short-term transients, exclusion of artifacts of the laboratory environment and applicability to the range of water flow rates and surface-to-volume ratios under repository conditions. The latter condition is due to the importance of flow rate and dilution in determining long-term dissolution rates and mechanisms. Accordingly, continuous- or pulsed-flow tests, especially those carried out in controlled environments and at relatively slow flow rates, are most useful in providing a data-base for the characterization of long-term durability. At very high flow rates constant-medium, frequent-exchange tests of the IAEA type determine the limiting leach rates in the incoming water composition unaffected by the presence of the glass. At the low-flow-rate limit, long-term stagnant tests using very high surface-to-volume ratios are very useful in evaluating ultimate pH values and solubilities. The results of ordinary static tests at low S/V ratios are highly influenced by short-term transients, and data based on such tests only approach convergence with results of dynamic tests if the tests are carried out for very long periods of time.

1.3.1 General

On the basis of the considerations detailed in the previous section it can be concluded that in simulating repository conditions for durability evaluations the ranges of glass and leachant compositions and of temperatures are fairly well defined. One of the most important variables to be explored over a broad range of values is the rate of leachant flow, while the other parameter which is involved in determining contact time, viz. the surface-to-volume ratio, has moderately high to very high values.

Several different types of test methods have been applied to the study of waste form materials (Mendel 1973; Barkatt et al. 1981).

1.3.2 Constant-Medium Tests

The first type of test consists of those tests which characterize the leach behavior in the short-contact-time, noninteractive case, which involves rapid leachant exchange and high dilutions. Such tests include the IAEA method (Hespe 1971), the ISO method (International Standard 1980) and variations on these tests. The surface-to-volume ratios employed are typically 10 m^{-1} (International Standard 1980), or $>10\text{ m}^{-1}$ (Hespe 1971), and the entire leachant is typically changed at intervals which increase from 1 to 30 days (International Standard 1980) or 1 to 180 days (Hespe 1971) in the course of the test. These arbitrary guidelines are not sufficient to ensure that the accumulation of leach products, such as alkalis and saturating species (e.g., Si, Al) will not affect the leach rates, especially when elevated temperatures and samples with low durabilities are involved. This problem has been recognized by Soper et al. (1983), who found it necessary to shorten the test duration from 3 days to 1 day and reduce S/V by a factor of 4 when carrying out leach tests at 90°C on powdered borosilicate defense waste glasses, even though the leachants were buffered. Generally, it is necessary to use buffered media (Barkatt et al. 1981; International Standard 1980) and keep the leachate concentrations far below saturation limits (e.g., below 5 mg/L Si and below 0.5 mg/L Al) (Barkatt et al. 1981) in order to ensure that the test is indeed noninteractive. The results of such a test can be shown to reflect a constant leach rate characteristic of constant-medium conditions if upon further decrease in leachant exchange frequency or in S/V the observed leach rates remain unchanged. Soxhlet-type tests, such as the MCC-5S method (Materials Characterization Center 1981), also belong to this class of

tests, but they are limited to the use of pure or azeotropic liquids at the boiling point corresponding to the pressure used in the test, and most usually to the use of pure water at 100°C.

1.3.3 Solubility Tests

In order to characterize the behavior of glasses in the fully interactive, saturated case and to quantify the pH and solute concentrations which result at very long contact times, it is necessary to use tests which employ conditions opposite to those described above, i.e., very long immersion periods, very high S/V ratios, and the exclusion of external buffering agents. The MCC-3S agitated powder method (Materials Characterization Center 1981) belongs to this class of tests, especially if carried out over long periods of time. If, upon prolonging the immersion time or further increasing S/V, leachate concentrations remain unchanged, the test results can be considered to reflect the leach behavior in the saturated region.

The preferred method of determining solubilities is to approach equilibrium saturation from subsaturation (isothermal dissolution) and from supersaturation (after presaturation at a higher temperature or solvent evaporation) until the compositions obtained using the two methods become similar. In the case of waste glasses such as PNL 76-68 large discrepancies between the results of these two methods were found even after one year (Fullam 1982) due to the possible effects of slow dissolution kinetics, persisting supersaturation, colloid formation, pH differences (possible CO₂ penetration) and the dependence of solid phase composition on temperature (see 1.3.9).

1.3.4 Flow Tests

The test methods described in the previous two paragraphs can be used to obtain data about the leach behavior of the waste form under limiting conditions of very rapid flow or no flow at all. However, the first case is unlikely to occur in geologic repositories (although it may occur in accident scenarios) and, in the second case, if both mass flow and diffusion are absent, no material loss from the repository due to leaching needs to be considered. As detailed in paragraph 1.2.3 and in Chapter 3, the most interesting conditions involve moderately slow flow rates. Since it is necessary to explore the behavior of the system at long times, flow tests must be continued until the composition of the aqueous phase becomes nearly constant. The resulting concentrations can be taken to

represent the leach behavior at a contact time which corresponds to the flow rate and S/V ratio employed in the test.

1.3.4.1 Continuous-Flow Test Methods

Several dynamic test techniques have been proposed. One of them is represented by the MCC-4S "low-flow-rate" method (Materials Characterization Center 1981) as well as by various other flow tests, conducted with a single pass of the leachant through the leach vessel (Coles et al. 1979).^(a) This technique has been extended to develop elaborate systems which involve a flow of ground water through fissured rock specimens in combination with a simulated repository vessel containing glass and metal samples in a radiation/elevated temperature environment (Seitz, Bowers and Fortney 1981). Another approach involves multipass flow, i.e., recirculation of the leachant over a sample at a typical rate of 250 mL/min (Paige 1966; Clark et al. 1984). This is actually a stirred leachant test method, where the physical effects of flow are present but the flow rate is not directly related to the rate of leachant exchange in the repository.

Single-pass continuous-flow tests are typically carried out at volume flow rates of 34 to 185 mL·d⁻¹, corresponding to linear flow rates of 24 to 131 m·yr⁻¹ (Coles et al. 1979). More recent test procedures employ lower flow rates of 1.4 to 144 mL·d⁻¹ (Materials Characterization Center 1981), but the corresponding S/V ratio is relatively low (10 m⁻¹) compared with the S/V ratios most likely to be encountered under repository conditions (cf. Section 1.2.3). As detailed in 1.2.3 and in Chapter 2, the lower limit of these experimental flow rates just overlaps with the highest flow rates expected in a geologic repository.

Figure 1.1 illustrates the experimental setup of a single-pass flow test currently used by Clark and coworkers at the University of Florida.^(a) Deionized water equilibrated with the atmosphere (pH = 5.6 at 25°C) is passed from a large reservoir via a peristaltic pump through a polytetrafluoroethylene cell containing the glass (inside an oven) and finally into a polyethylene collection container. The flow rate through the cell may be varied from 0.1 mL/hr (=1 L/yr) to several hundred mL/hr, or the pump may be removed from the system to provide a static test. The

(a) A. R. Jurgensen and D. E. Clark. "Effects of Flow on Glass Corrosion." In preparation.

FIGURE 1.1. Experimental Configuration of Continuous-Flow Leach Test

volume of the cell and the sample surface area can also be changed. These options give a wide range of S/V ratios and residence times (i.e., the time required to completely replenish the solution in the corrosion cell). This test is similar to the single-pass MCC-4S flow test (Materials Characterization Center 1981) mentioned above. Solutions are collected and analyzed for pH and composition at regular intervals depending on the flow rate. Mass loss and surface analyses are also performed on samples after they are removed from the system. For rapidly flowing conditions (>1 mL/hr) the temperature of the oven is increased to give the desired temperature inside the corrosion cell. It should be emphasized that when this technique is used large amounts of CO_2 are present in the system due to the initial equilibration of the leachant with the atmosphere followed by the use of a flow and collection system which permits significant penetration of air. As a result, any pH excursions due to alkali leaching are suppressed to a large extent and the solubilities and dissolution rates of Si,

Al, etc., retain their low values characteristic of the near-neutral pH range.

1.3.4.2 Pulsed-Flow Test Methods

Since it is very difficult to use slower flow rates in a continuous flow experiment, a dynamic test based on a pulsed-flow concept, i.e., exchange of a relatively small fraction of the volume of the leachant at fixed intervals, has been developed (Barkatt et al. 1983a; 1981). Using this method (Figure 1.2), it is possible to achieve very low effective experimental flow rates (e.g., by replacing 5 mL of leachate with fresh leachant every 50 days the experimental flow rate becomes 0.1 mL/day) and to use very high S/V ratios in order to explore effects at very long contact times. Furthermore, it is much easier to control contamination of the system with CO_2 , O_2 , dust particles, etc., than in the case of a continuous flow system. Using this method with powder samples (to obtain high S/V ratios) it was possible to determine the effects of flow at equivalent rates as low as 0.03 m/yr (see below). The use of the S/V

FIGURE 1.2. Experimental Configuration of Pulsed-Flow Leach Test

ratio to scale effective contact times and the use of powders to obtain high S/V ratios are discussed in Sections 1.3.5 and 1.3.6.

1.3.4.3 Test Methods and the Evaluation of pH Effects

The mechanism of glass leaching at intermediate and low flow rates becomes controlled by the phenomena of pH drift and saturation. As detailed above (1.2.4), the pH has a very strong effect on dissolution rates of glasses as well as on solubility limits. Two experimental approaches to the study of leaching in this region have been pursued. One of them isolates the effect of saturation on leach kinetics through the use of buffers (most commonly, atmospheric CO_2) to keep the pH of the system at near-constant, near-neutral values. Due to the low saturation levels of Si, Al, etc., in this range saturation under these conditions can be observed and quantitatively analyzed at relatively high flow rates. The other approach is to allow both effects to take place by isolating the leach system from the environment, exploring the onset of saturation at the higher pH levels obtained as leached alkalis accumulate in the aqueous medium. In this case saturation-controlled behavior appears at much higher concentration levels. Together, the two approaches have been used to quantify the effect of changing leachant composition at slower flow rates on leaching kinetics and surface alteration.

Among the test methods used to characterize the dissolution of nuclear waste glass, the

IAEA-type constant-medium tests (1.3.2) provide for little or no change in the pH since they are designed to measure durability at very short contact times. Solubility tests (1.3.3) can reflect the full pH rise expected at long contact times since S/V ratios used in these tests are very high and the amount of leached glass components is sufficient to overwhelm the effect of CO_2 introduced at the beginning or in the course of the test unless the rate of gas leakage is very high. Static tests of the MCC-1 type (1.3.8), which specify low S/V ratios, however, usually reflect only a part of the pH rise expected in the absence of CO_2 and other buffering species originating in the test environment unless special precautions are taken to control and minimize the levels of such species.

The distinction between nonbuffered and significantly buffered test environments is particularly prominent in the case of the two types of flow tests described above. The pulsed flow test (1.3.4.2) is carried out under conditions which provide for almost complete exclusion of CO_2 and acidic components of the container material. Accordingly, the pH increase corresponding to the leaching of alkalis from the glass proceeds in full and the resulting rise in solubilities of Si, Al, etc., can prevent the onset of saturation except in the case of extremely long contact times. On the other hand, the continuous flow test (1.3.4.1) is carried out in an open system which permits large concentrations of CO_2 to dissolve in the leachate, suppress the pH excursion and cause the system to exhibit the effects of saturation even at relatively short contact times.

1.3.5 Effects of the Surface-to-Volume Ratio

As mentioned above, the use of high S/V ratios is the most practical way of exploring behavior at the long contact times which are usually expected under repository conditions. The use of S/V as a scaling factor for adjusting contact time values is based on the following argument. When a flow experiment conducted with a particular value of S/V and a contact time T_r is carried out until steady-state conditions have been reached, the normalized leach rates of each species will be characterized by a value L_i . This value reflects the pH and the solute concentrations in the solution which has a contact time T_r . The concentration of the corresponding species in the leachate is C_i , which is related to L_i through the equation

$$C_i = L_i(C_1, C_2, \dots, C_i, \dots, C_n) \sigma_i \frac{S}{V} T_r \quad (1.7)$$

where σ_i is the weight fraction of the component i in the waste form and $C_1, C_2, \dots, C_i, \dots, C_0$ are the concentrations of all the species in the aqueous phase (including H^+ and OH^-).

As long as L_i depends on the composition of the aqueous phase and does not depend explicitly on S/V , it can be seen that identical values of C_i are obtained when both S/V and T_r are varied as long as

$$(S/V)_1(T_r)_1 = (S/V)_2(T_r)_2 \quad (1.8)$$

If $(S/V)_2$ is taken to represent an expected value of the S/V parameter in the repository, then the leach rates characterizing the contact time $(T_r)_2$ in the repository environment can be determined by carrying out an actual test with an experimental contact time of $(T_r)_1$ (reciprocal of the exchange frequency) and using an experimental ratio $(S/V)_1$ as required by eq. (1.8). Large values of $(S/V)_1$ can be used to predict the leach behavior at very slow flow rates and long $(T_r)_2$ in the repository. Eq. (1.8) can be expected to hold at all flow rates as soon as the leach rates cease to be significantly time-dependent. At very short total exposure times, when leachate concentrations are still dependent on $t^{1/2}$ and the leach rates are explicitly proportional to $t^{-1/2}$, the values of L_i will depend on time and on S/V individually (Machiels and Pescatore 1982).

Ethridge, Clark and Hench (1978) demonstrated that the time required to reach a specific concentration of glass constituent in solution is indeed inversely proportional to S/V over broad ranges of the latter parameter. The characteristic time required for the linear corrosion ($C \propto t$) rate law to become predominant is also inversely related to S/V . The experiments involved did not show any evidence of saturation. Oversby (1982) showed that the leach rates for different sample geometries or leaching times are comparable at equal values of $(S/V) \cdot T_r$ in the saturation-precipitation region. Bates and Steindler (1983) showed that a high S/V ratio accelerates the saturation process and permits alteration products to form more rapidly on the glass surface. Pederson et al. (1983) concluded that glass leaching data for a range of leaching times and S/V values can be represented by a single curve when plotted against the product of S/V and T_r , with the possible exception of cases where colloid formation and certain alteration phase formations take place in multicomponent systems. As shown in Sections 1.4.3.1 and 1.4.3.2, results of both continuous-flow and pulsed-flow tests carried out with various

combinations of S/V and T_r show that eq. (1.8) is validated in the slow-flow (saturation) region as well as in the rapid-flow (corrosion) region.

1.3.6 Block and Powder Tests

Until recently, the general tendency in tests aimed at the determination of leach rates was to rely exclusively upon data obtained with regular block samples with well-defined geometric surface areas and to exclude powder tests (except in solubility studies) due to uncertainties in the determination of powder surface areas and possible powder stacking effects. However, in attempting to use high experimental S/V ratios in order to explore leach behavior at long contact times (see 1.3.5) it proves to be extremely difficult to increase S/V beyond about 300 m^{-1} while maintaining free water circulation in the leach vessel. Moreover, recent work has shown that the quality of the surface finish has a strong influence on the observed leach rates of macroscopic samples, at least at short times (see Chapter 2). For instance, Wallace and Wicks (1983) noted that in MCC-1 tests on defense waste glass a very rapid leaching process takes place within the first few days and that the extent of this rapid process is highly irreproducible and is related to the nature of the initial surface. On the other hand, powder grains have fractured, rather than machined, surfaces, and considerable progress has been made in obtaining reliable specific areas of powder for leaching purposes. Several independent studies indicate that the specific surface areas of powders (e.g., -42+60 mesh size) are much smaller than the BET nitrogen adsorption area, $0.0260 \text{ m}^2/\text{g}$ (Hollis 1976), for glasses with densities of 2.5 to 3.0 g/mL . This is due to the fact that access by solution and free transport of ions from the surface to the bulk solution require much larger pore areas than gas adsorption (Flynn, Jardine and Steindler 1979). The specific areas for a larger number of both artificial (nuclear waste) and natural glasses and crystalline solids were determined by leaching powdered samples under high-dilution, frequent-exchange conditions and comparing the results with leach data obtained on small, highly polished specimens with a regular geometric shape. The amount of powder was adjusted in each case to provide leachate concentrations close to those obtained with the polished specimens. The resulting values for the specific surface areas of the -42+60 mesh powders are in the range of $(0.025 \pm 0.004)/\rho \text{ m}^2 \cdot \text{g}^{-1}$, where ρ is the density of the material (Barkatt et al. 1984a; 1983; 1981). For nuclear waste glasses the value

is $(0.0097 \pm 0.0011) \text{ m}^2 \cdot \text{g}^{-1}$. The specific area for leaching agrees much better with a calculated value of $0.007 \text{ m}^2 \cdot \text{g}^{-1}$ based on spherical geometry (Soper et al. 1983; Ethridge, Clarke and Hench 1978; Barkatt et al. 1981; Oversby 1982). As shown below the leach rates of powders measured during the later stages of dynamic tests conducted using high S/V ratios agree very well with the leach rates of blocks when specific powder areas based on the results of high-dilution (low S/V) tests are used. However, marked differences between powdered samples and blocks are observed upon monitoring leachate concentrations as a function of time. In the case of powder tests the leachate concentrations gradually approach the steady state values in agreement with predicted time-dependence curves based on the assumption of constant leach rates. On the other hand, in the case of ground and polished samples leachate concentrations are initially much higher, probably due to the uneven and unstable character of ground and polished surfaces compared with fractured ones. Tests using powdered samples can be carried out with S/V ratios of at least $2 \times 10^3 \text{ m}^{-1}$ without significant discrepancies due to stacking effects, as shown by the fact that the leachate concentrations throughout the entire course of the test still depend only on the $(S/V) \cdot T_r$ product and exhibit the same values when this product is maintained unchanged even when different individual values of (S/V) and of T_r are used (see 1.4.3).

1.3.7 Pulsed-Flow and Continuous-Flow Experiments

In a typical continuous-flow experiment, water flows through a 100 mL leach vessel at a rate of 2.5 mL/day. In a corresponding pulsed-flow experiment carried out in a similar vessel and with the same sample composition and configuration, S/V ratio and temperature, 25 mL of leachate may be withdrawn every 10 days and replaced with fresh leachant. In order to apply the pulsed-flow technique to the leach behavior under flow conditions it was necessary to show that the periodic rapid exchange of a fraction of the leachant does not perturb the glass-water interacting interface to produce different effective leach rates than those prevailing when the leachant is changed slowly and gradually. The results of two sets of dynamic tests are given in Tables 1.2 and 1.3. In the first set of experiments the pulsed-flow technique was used and the exchange interval and the exchanged volume were varied while leaving their product (the effective flow rate) unchanged. The results show that under these conditions the compositions of the

TABLE 1.2. Correlation of Exchanged Fraction and Exchange Frequency, PNL 76-68 Glass, 70°C

Ionic Composition of Flow Experiment Leachates

S/V, m^{-1}	825	825
Total Volume	100 mL	100 mL
Exchange Volume	25 mL	7.14 mL
Exchange Interval (Δt)	7 days	2 days
Residence Time (T_r)	28 days	8 days
<u>Cations, mMole/L</u>		
<u>Leach Products</u>		
Na^+	5.62	5.04
Cs^+	0.02	0.02
H_3O^+	1×10^{-7}	1.7×10^{-7}
Total Cations	5.64	5.06
<u>Anions, mMole/L</u>		
<u>Leach Products</u>		
H_3SiO_4^-	1.86	1.94
$2 \times \text{H}_2\text{SiO}_4^{2-}$	0.06	0.06
H_2BO_3^-	2.80	2.48
$2 \times \text{HBO}_3^{2-}$	0.01	0.01
$2 \times \text{HPO}_4^{2-}$	0.13	0.11
OH^-	0.09	0.07
<u>Others</u>		
HCO_3^-	0.05	0.07
$2 \times \text{CO}_3^{2-}$	0.05	0.06
F^-	0.02	0.11
Total Anions	5.07	4.91

leachates obtained in the two experiments (after a large number of exchanges in each test) were identical within experimental error. The second set of values, which consists of an interlaboratory comparison of the results of a continuous-flow test and pulsed-flow test carried out on DWRG at 90°C under similar conditions (90°C , $S/V = 10.0$ to 10.7 m^{-1} , $T_r = 25$ to 28 days), shows that the leachate concentrations obtained in the pulsed-flow test are approximately twice as large as those observed the continuous-flow test. This difference can be directly attributed to the higher pH reached in the pulsed-flow test (see Table 1.3) due to the

TABLE 1.3. Comparison of Continuous-Flow^(a) and Pulsed-Flow^(b) Leach Tests in Deionized Water at 90°C

Stabilized Leachate Concentrations, mg/L		
	Continuous-Flow	Pulsed-Flow
total time = 84 days		
pH	7.3	8.91
Si	5.79	12.54
Li	0.69	1.31
Na	1.75	3.88
total time = 105 days		
pH	7.36	8.93
Si	5.11	12.90
B	0.75	1.40
Li	0.79	1.26
Na	1.34	3.67

- (a) Continuous-flow experiment, University of Florida.
 (b) Pulsed-flow experiment, The Catholic University of America.
 (c) MCC DWRG, 13-mm, 600-grit-surface cubes, $S = 1.00 \times 10^{-3} \text{ m}^2$, $V = 1.00 \times 10^{-4} \text{ m}^3$, $S/V = 10 \text{ m}^{-1(a)}$, $10.7 \text{ m}^{-1(b)}$, $T_r = 25 \text{ days}^{(a)}$, $28 \text{ days}^{(b)}$

more effective exclusion of CO_2 from the pulsed-flow system (cf. 1.3.4.3). Even larger differences between results of the two tests may be expected at longer contact times where the pH rise, if not suppressed, is more pronounced.

1.3.8 Static Tests

A large number of the leach tests employed at the present time consist of static techniques based on the MCC-1 test method (Materials Characterization Center 1981), which specifies the use of monolithic samples, an S/V ratio of 10 m^{-1} and a single leaching interval with no intermediate leachant sampling or exchange, although the use of several different test durations is recommended, each applied to a different sample. The test has been shown to be relatively simple and useful in the comparison of various waste forms (Stone 1982). Several models have successfully accounted for the short-term dependence of MCC-1 results on test duration, i.e., for

the initial $C \propto t^{1/2}$ behavior and the transition to the $C \propto t$ rate law (Kuhn and Peters 1982; Machiels and Pescatore 1982; Wallace and Wicks 1983). However, it is difficult to apply the results of such static tests directly to the identification of the controlling mechanisms and the prediction of leach behavior under flow conditions, where the long-term, stabilized leach rates characterize the extent of corrosion. This is due to the absence of leachant exchange, the retention of leaching products obtained during the earliest stages of the exposure when leach rates heavily depend on surface preparation, (see Section 1.3.6 and Wallace and Wicks 1983) and the small S/V ratio. However, if a static test is continued for a sufficiently long time until the saturation-precipitation region is reached and the relative importance of early leaching to the leachate composition decreases, the leachate concentrations obtained in static tests begin to approach those obtained in dynamic tests with similar values of $(S/V) \cdot T_r$. (In the case of a static test the total exposure time is used for T_r .) Under these conditions, the release rates (based on eq. 1.7) obtained in the two tests will also begin to converge (see Section 1.3.5). The convergence between the two types of tests will occur earlier when high S/V ratios are used (Oversby 1982). In general, when the leach rates are expressed as a function of time the results of leach tests are found to be highly sensitive to testing conditions. However, it is also possible to express these results as a function of the concentration of leach products, which is an indicator of the progress of the leaching process (cf. Section 1.3.5 and eq. 1.7). Using this approach it can be shown that the results of replenishment tests, such as those described in 1.3.4, at increasing slow flow rates approach the results of static tests in which the pH is preadjusted at its final steady-state level (Harvey 1983). A detailed comparison between the results of the MCC-1 static test and those of the pulsed-flow dynamic in the case of the Defense Waste Reference Glass is given in Section 1.5.8 and Table 1.14.

1.3.9 Accelerated Tests

As mentioned above, the interaction of nuclear waste glasses with aqueous media is a complex and slow process and long-term, slow-flow data is difficult to obtain under laboratory conditions, especially at low temperatures (Fullam 1982). Several methods have been used to explore the long-time, saturation-controlled characteristics of the leaching process.

(a) S/V Acceleration

High S/V ratios can be used to study the effects of long contact times as long as $(S/V) \cdot t_r$ normalization is valid (see 1.3.5).

(b) Chemical Acceleration

The two principal effects of long-term interaction with the glass on the reactivity of the leachant are due to a rise in pH and to the accumulation of scarcely soluble products (Si, Al, etc.). Following determination of the limiting pH by means of solubility tests (see 1.3.3) it is possible to avoid complications due to a continuously changing pH by using leachant solutions containing alkalis (Soper et al. 1983; Harvey 1983) or alkaline buffers (Barkatt et al. 1981) adjusted to the final pH values. It is also possible to add saturating leach products such as Si, Al and Fe to the leachant composition (Hermansson et al. 1983). As expected, aqueous media enriched in NaOH give rise to higher leach rates than those observed in deionized water while corrosion in high-silicate water is slower. Accordingly, the use of leachants prepared in advance with the expected steady-state concentrations of the leach products can lead to rapid characterization of long-term leach rates although it does not provide information on the evolution of these rates with exposure time.

(c) Temperature Acceleration

The use of higher temperatures to accelerate the dissolution processes and provide early information about long-term durabilities requires careful analysis of the mechanisms involved. For instance, if leach tests are carried out over the same period of immersion at several temperatures, the release rates observed at the lowest temperatures may be controlled by matrix dissolution or hydration with a high kinetic activation energy (typically around $80 \text{ kJ} \cdot \text{mol}^{-1}$). The release rates at intermediate temperatures may be controlled by saturation (characterized by relatively low enthalpies, typically around $15 \text{ kJ} \cdot \text{mol}^{-1}$). The results obtained at the highest temperatures may reflect the formation of crystalline alteration products. The nature of these products is also temperature-dependent (Fullam 1982). Accordingly, simple Arrhenius-type extrapolations cannot be used in general unless the mechanism of

water/glass interaction over the test period has been proved to be unaffected by temperature within a certain range. However, tests at elevated temperature can be applied to long-term leach behavior when a single process involved in the interaction between glass and water (e.g., matrix corrosion, saturation or crystallization) is considered. Thus, by following the crystallization of the leached surface layer of nuclear waste glasses, the time required for this particular process to take place was found to be a smooth function of temperature, without any observed breaks between room temperature and the hydrothermal region (see 1.4.5, 1.5.10 and Chapter 4). Using this approach, high-temperature tests (Bates and Steindler 1983; McCarthy et al. 1978) can indeed serve to provide information about long-term leach processes and leach products at lower temperatures.

1.4 EXPERIMENTAL FINDINGS AND INTERPRETATION: SRL TDS-131 GLASS

SYNOPSIS

Various leach tests carried out on SRL TDS-131 Defense Waste Glass led to the following conclusions:

- (a) *Diffusion-controlled surface hydration controls the leaching process only during the first few days of exposure and is not rate-controlling in the long term, where the rate of material loss becomes constant.*
- (b) *At high flow rates the controlling mechanism is simple corrosion. This process is, to a good approximation, both linear with time and congruent, since the leach rates of the matrix elements (Si, Al) are similar to those of the leaching of the alkalis and of boron. A gel layer which contains the insoluble glass components (e.g., Fe, Mn, Ni) is formed, but it is too porous and too permeable to control the leach kinetics.*
- (c) *At slow flow rates (below 1 m/yr) leaching becomes controlled by saturation and formation of alteration products. The leach rates decrease in the course of slow-flow tests before apparently leveling off at constant values which are almost inversely proportional to the contact time, indicating that leachate concentrations have become solubility-limited. The low concentrations observed at this stage in the leachate indicate*

the formation of more stable, less soluble alteration products. The fact that even the concentrations of the most soluble glass components (e.g., boron) level off indicates that the altered surface layer is protective in retarding the dissolution process. Al and most of the Si are redeposited in the surface layers (i.e., the alteration layer and the gel layer) under slow flow conditions, and therefore the steady-state concentrations of Si and Al are lower than those of B, Na and Li although all of these elements are probably dissolved from the original glass at the same rate. The composition of the layer deduced from solution analysis and mass balance agrees well with findings concerning the alteration products based on surface spectroscopy.

- (d) The pH rise observed upon leaching TDS-131 glass is extremely large, reaching values as high as 12.4 in the case of prolonged powder solubility tests. The sharp rise in solubilities with increasing pH causes the transition from corrosion-controlled to saturation-controlled behavior to occur only at low flow rates, and causes leachate concentrations to rise slowly with decreasing flow rate even in the solubility-controlled region. On the other hand, when the pH rise is suppressed, saturation effects are observed even at high flow rates. In laboratory tests the most common cause of the suppression of pH excursion is the presence of external buffers, such as CO_2 ($\text{pK}_{\text{H}_2\text{CO}_3} = 6.37$), which prevents the dissolution rates and solubilities of silica, alumina, etc. from rising when leached alkaline species accumulate in the solution.
- (e) That the length of time elapsed in slow-flow experiments at 70°C before saturation with respect to alteration products becomes the mechanism which controls silica levels, correlates well with extrapolation of the times required for the appearance of crystalline phases at higher temperatures. Apparently, the control of leachate concentrations by the altered surface is triggered by the onset of alteration and reprecipitation of the matrix elements, which occurs earlier than full development of crystalline phases.
- (f) Higher temperatures promote both the approach to saturation under given flow/dilution conditions and the formation of alteration products.

- (g) The effect of substituting ground water for deionized water on leach rates is similar to the effect of leaching at lower flow rates, and both effects stem from the lowering of leach rates at higher silicate concentrations and more moderate pH levels. However, at long contact times the large pH rise which results from the extraction of alkalis from TDS-131 glass minimizes the retarding effect of the presence of silica (in the initial ground water composition) on the leach rates.

1.4.1 General

TDS-131 glass is not considered a reference defense waste form, but in view of the extensive data base available for this glass, and the conclusions about glass composition effects provided by comparing findings obtained on TDS-131 with those obtained on MCC DWRG, the results of studies on this glass are described before a discussion of the data obtained so far for DWRG.

1.4.2 Short-Contact-Time Tests

A replenished frequent-exchange test, based on IAEA (Hespe 1971) and ISO (International Standard 1980) procedures, was carried out on a rectangular sample in deionized water at a temperature of 90°C . The S/V ratio was 10 m^{-1} , and the water was replaced daily for the first 5 days, weekly for the next 2 weeks, and every 2 weeks thereafter. The results of the test are shown in Figure 1.3. They indicate that after the first 5 days, and for a period of at least 2 years, the slope of the logarithmic plot of material loss versus time has a constant value of (0.90 ± 0.05) for Si and B as well as for Na. This indicates that under the conditions of the test a matrix dissolution mechanism is apparently the controlling mechanism of the attack of water on the glass almost from the beginning of the test, since a mechanism which entails diffusion across a protective layer would have resulted in a slope of 0.5 (Holland 1966). (The fact that the slope is 0.9 rather than 1.0 is probably related to the retention of minor insoluble glass components on the leached surface, see below.) Another indication that classical selective alkali leaching is not the controlling mechanism is furnished by the observation that from the beginning of the test the normalized leach rate of boron is as fast as that of sodium. This was also noted in static MCC-1 tests (Wallace and Wicks 1983). The nonprotective character of the surface formed at short contact times is also reflected in the

FIGURE 1.3. Results of Frequent-Exchange Tests on SRL TDS-131, Deionized Water, 90°C

lack of a large drop in leach rates in the case of pre-corroded specimens [Sales, Petek and Boatner 1983; J. K. Bates^(a)].

1.4.3 Flow Tests

In order to characterize the leach behavior of nuclear waste forms under the various flow conditions which may be expected in a geologic repository, the dynamic leach test (described in Section 1.3.4) was used. Two sets of results were obtained. The first was obtained using the continuous flow test method (1.3.4.2), which was mostly confined to high flow rates. Most important, the pH rise in this test was largely suppressed due to the fact that CO₂ had access to the system. Accordingly, pH levels remained low and so did the solubilities and dissolution rates of silica, alumina, etc. The second set of data was obtained using the pulsed-flow test method (1.3.4.3) which can be used to explore slow-flow behavior and which permits the effects of the full pH excursion to be studied.

1.4.3.1. Continuous-Flow Tests

An extensive matrix of flow experiments has been carried out by Clark and coworkers at the University of Florida in the case of SRL

TDS-131 simulated waste glass.^(a) The composition of this glass, which is made up of SRL Frit 131 +29.8% simulated TDS waste, is given in Table 1.1. The experimental set-up has been described in 1.3.4.1 and in Figure 1.1. The flow rate was varied from 0 (static) to 50 mL/hr while maintaining a constant temperature of 90°C, S/V = 10 m⁻¹, the cell volume was varied from 30 mL to 60 mL, and the glass sample surface areas were varied from 3 x 10² mm² to 6 x 10² mm². The variations in these experimental parameters provided indications of their relative importance in glass corrosion as well as an evaluation of the effects of flow rate in near-neutral aqueous environments. Selected values for each of these variables were then used to compare the defense waste reference glass (DWRG) to the SRL TDS-131 glass (cf. 1.5.3.1) as well as to evaluate the effects of other system components such as leachant composition and the presence of iron (See Chapter 3). Parts (a) and (b) of Figure 1.4 illustrate the effects of flow rate on the Si concentration released from the sample. It can be seen that the concentration of Si decreases as the flow rate increases. Additionally, the Si concentration exhibits a maximum in most cases and then decreases to a constant value. The time required to achieve the constant value decreases as the flow rate increases. These transient changes are thought to be due to glass surface effects resulting from sample preparation. The system is assumed to be at steady state when the concentrations become constant with time. Concentrations of other elements such as Na, Li and B exhibit the same trends, as shown in part (c) of Figure 1.4. Of course their steady-state concentrations are different from those shown for Si. Temperature is also expected to influence the steady-state concentrations as well as the time required to achieve these concentrations. The steady-state concentrations should decrease and the time required to achieve steady state should increase as the temperature is reduced. About 28 days are required to reach steady state at a flow rate of 0.1 mL/hr and about 3 days are required for 50 mL/hr at 90°C, S/V = 10 m⁻¹. An extensive treatment of the effects of flow and water exchange rates on dissolution and of the distinction between the dissolution behavior in the saturation-controlled slow-exchange region and the kinetics-controlled rapid-exchange region has been carried out by Berner (1978) for the general case of mineral

(a) J. K. Bates. 1982. Private communication.

(a) A. R. Jurgensen and D. E. Clark. "Effects of Flow on Glass Corrosion." In preparation.

A).

B).

C).

FIGURE 1.4. Effects of Flow Rate on Leachate Concentrations Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131 Glass

dissolution. Effects of flow in models of glass dissolution are discussed in detail in Chapter 6.

Under saturated conditions, a change in flow rate should not result in a change in steady-state elemental concentrations measured outside the corrosion vessel. However, the elemental release rate should be directly proportional to the flow rate as long as solution saturation is maintained for the element of interest; i.e.,

$$\text{Release rate} = (\text{flow rate})(\text{saturation concentration}) \quad (1.9)$$

The flow rate represented in this equation is the volumetric flow rate. According to eq.

(1.9), a tenfold increase in flow rate should produce a tenfold increase in the release rate. In general, the data show that the release rate increases at a slower rate than the flow rate. When the flow rate is too great for saturation concentrations to be maintained inside the corrosion cell, the release rate should become constant and independent of the flow rate:

$$\text{Release rate} = (\text{flow rate})(\text{concentration}) \quad (1.10)$$

Under these conditions the solution concentration will be inversely proportional to the flow rate and a tenfold increase in the flow rate should result in a tenfold decrease in the solution concentration. Furthermore,

this condition corresponds to the maximum release rate from the glass. Leaching occurs as if the glass was immersed in an infinite volume of solution. A similar model involving a region in which the release rate is independent of flow rate has been developed by Hughes, Marples and Stoneham (1983). The transition from saturation-controlled release rate to flow rate independent release rate (i.e., from Region 1 to Region 2 in Figure 1.5) is expected to occur over a range of flow rates and to vary with element. As detailed below, the saturation concentration which appears in eq. (1.9) and the corresponding release rate under saturation-controlled conditions are independent of the surface area of the exposed glass. On the other hand, the constant release rate which prevails under rapid-flow, highly unsaturated conditions according to eq. (1.10) can be represented as the product of the specific leach rate for a unit area of the glass and the total exposed surface area. Under these conditions the concentration of the solution at steady state can be expressed by the equation:

$$\text{(concentration)} = \frac{(\text{leach rate})(\text{area})}{(\text{flow rate})} = \frac{\text{normalized leach rate} \times \text{elemental weight fraction} \times (\text{area})}{(\text{flow rate})} \quad (1.11)$$

There was no attempt to control the CO₂ concentration in the water for the experiments reported in this section. It is known that CO₂ can affect the leaching behavior of the glass by either buffering the pH of the solution (1.3.4.3) or by reaction with the rare earths present in the glass to form insoluble carbonates (cf. 1.4.7). The effects on leaching due to pH buffering by CO₂ are likely to be important even under high flow conditions, while the effects due to insoluble carbonate formation will probably be important under static and low-flow conditions.

Figure 1.5 illustrates the release rates of Si and Na as a function of flow rate. The concentrations used to calculate the release rates for Si are the steady-state concentrations shown in Figure 1.4. The steady-state concentrations in Figure 1.4 were used in eq. (1.11) to calculate the steady-state normalized release rates shown in Figure 1.5.

It can be observed that the release rate does increase up to a flow rate of about 10 mL/hr, at which point release rate becomes nearly independent of flow rate. Steady-state values were used to produce Figure 1.5 because the saturation values are dependent on the solution pH. The data presented in Figure 1.6 show that pH values, and thus the saturation concentrations, are very dependent

FIGURE 1.5. Effects of Flow Rate on the Release Rates of Si and Na in Continuous-Flow Leach Tests on TDS-131 and DWRG

FIGURE 1.6. Effects of Flow Rate on Leachate pH Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131 Glass

on the flow rate. Consequently, the value of solution saturation used in eq. (1.9) must be known for each of the steady-state pH values shown in Figure 1.6. Since the saturation concentration is dependent on the flow rate, the release rate defined in eq. (1.9) is not expected to be linear with flow rate.

The total weight loss based on weighing the sample before and after corrosion begins to level off after seven days of corrosion for the samples exposed to the static solutions and the solution with a flow rate equal to 0.1 mL/hr (Figure 1.7). As the flow rate increases, the sample weight loss increases at a more rapid rate after 7 days for flow rates greater than 0.1 mL/hr. The equivalent behavior during the first 7 days for all flow rates is presumably due to the fact that none of the solutions are near saturation, and hence solution concentrations are not suffi-

FIGURE 1.7. Effects of Flow Rate on Total Mass Loss Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131 Glass

cient to retard the release rates. Past 7 days the solution concentrations begin to assume major importance for the slow-flow and static solutions. The rates of release (i.e., slopes of curves in Figure 1.7) increase significantly for flow rates between 0.1 mL/hr and 10 mL/hr. However, for higher flow rates the release rates become nearly constant. This is consistent with the curve shown in Figure 1.5.

SEM-EDS observations are shown in Figure 1.8 for the 28-day corroded samples exposed to several flow rates. In general, the surfaces of the static and 0.1 mL/hr samples appear to be compositionally identical. However, significant compositional differences can be seen as the flow rate is increased up to 10 mL/hr. The thicknesses of the surface layers (used in this section synonymously with gel layer) are shown in Figure 1.9 for

a).

b).

c).

FIGURE 1.8. SEM-EDS of 28-Day Corroded Samples Exposed to Water at Several Flow Rates

FIGURE 1.8. (contd)

these glass samples as well as glass samples exposed to other conditions of flow. In general, the thickness of the gel layer (determined by SEM) increases as the exposure time increases and as the flow rate increases up to 10 mL/hr. Note that the rate of increase in thickness becomes constant for flow rates greater than 10 mL/hr. This is consistent with the data shown in Figures 1.5 and 1.7. Differences in gel layer thickness were also obtained by varying the S/V ratio while maintaining other conditions constant. It can be seen that doubling the S/V ratio at a flow rate of 0.5 mL/hr resulted in reducing the gel layer thickness by a factor of nearly 2

(i.e., from 5 μ m to 3 μ m). Additional discussion of layer composition and morphology is presented in Chapter 2.

Figure 1.10 illustrates the effects of varying the flow rate and the S/V ratio while maintaining a constant contact time. Doubling the S/V ratio by doubling the surface area of the glass, while maintaining a constant cell volume, results in about a twofold increase in the release from the entire glass sample for any given flow rates within the range investigated here. Doubling the volumetric flow rate while maintaining a constant S/V ratio slightly more than doubles the

FIGURE 1.9. Thickness of Leached Layers Observed in 28-Day Corroded Samples Exposed to Water at Several Flow Rates

FIGURE 1.10. Effects of Flow Rate and S/V on Total Mass Loss Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131

total release from the entire sample area. Doubling the flow rate while maintaining a constant sample surface area (and reducing S/V by a factor of 2) does not appreciably affect the total release. These results suggest that the contact time is more important than either S/V ratio or flow rate. Hughes, Marples and Stoneham (1983) state that sample surface area should be unimportant under conditions of saturation. However, surface area should affect the flow rate at which the release rate becomes constant. Since in the present case the total release is proportional only to surface area and is insensitive to changes in both flow rate and S/V ratio, it can be concluded that the release rate per unit area [as defined in eq. (1.11)] is, to a good approximation, constant. Accordingly, it appears that these conditions of flow correspond to Region 2 on Figure 1.5. The thicknesses of the leached layers formed on selected glasses from this experiment are shown in Figure 1.9.

It should be noted that, as stated above (cf. 1.3.4.2), the leachate concentrations observed in the continuous flow test, which is carried out in an open system, are strongly influenced by leakage of CO_2 into the solution, resulting in attenuation of the rise in pH. Since this process is dependent on time only, it can account at least in part for the observation that deviations from sole dependence of leach rates on $T_r \cdot (S/V)$ are observed (cf. 1.3.5). This problem is not encountered in the controlled-environment pulsed-flow tests as detailed in the next paragraph. At very high flow rates, where large pH excursions are not expected to occur even in the absence of CO_2 , the results of the two types of flow tests can be expected to approach similar values.

1.4.3.2 Pulsed-Flow Tests

In order to study the leach behavior of SRL TDS-131 glass over a broad range of flow rates, including the slow rates most likely to characterize geological repository conditions, and in order to study the leach behavior in an environment free of the presence of external buffers (such as CO_2), the pulsed-flow test described above (1.3.4.3) was used. This method is based on a replacement of a constant fraction of the leachate in contact with the solid sample with fresh leachant at fixed intervals (Barkatt et al. 1981). When the leachate concentrations monitored in such a test, or in any properly controlled flow test, are observed to approach levels which remain constant in time, these concentrations can be used to derive long-term release rates at a certain contact

time or rate of leachant exchange. This rate can be converted into the flow rate of water through a repository using the geometric parameters of the repository (Barkatt et al. 1983a).

This test is a particularly useful diagnostic for leach mechanisms, since there are several independent features of the test data which are indicative of the controlling mechanism. These features include the dependence of the leachate concentrations on time until they approach constant levels, the dependence of the final concentrations themselves on the contact time T_r at a given S/V, i.e., on the effective flow rate, and the relative leach rates of various glass components. Figure 1.11 represents the use of measurements of leachate concentrations as a function of actual exposure time (i.e., time elapsed from the beginning of the test) to identify controlling mechanisms in the case of a test carried out at a particular flow rate. In the case that the controlling mechanism is diffusion through a layer, leachate concentrations initially rise with time and then decrease as a protective layer builds up, slowing down the leaching process. In cases where the controlling mechanism is simple corrosion (matrix dissolution at constant rate) or saturation, leachate concentrations steadily rise with time until they approach constant levels. In the case of saturation these final levels are independent of the flow rate, while in the case of simple corrosion the steady-state concentrations are inversely proportional to the flow rate (Figures 1.12 and 1.13). The relative magnitudes of the normalized leachate concentrations or normalized leach rates of various glass components observed in dynamic leach tests can also be used to distinguish among various possible controlling mechanisms (Figure 1.14). In the case of simple corrosion, the normalized release rates of all major glass components, including the alkalis, B, Si and Al are nearly the same. In the case of diffusion-controlled hydration the most mobile ions, i.e., the alkalis, should have the highest leach rates. In the case of saturation, relative release rates are controlled by solubilities and boron, which has the smallest tendency to form insoluble compounds, is most rapidly released. Only those elements which are highly insoluble at neutral and moderately basic pH levels, such as Fe, Mn and Ni, have very low release rates regardless of the mechanism.

(a) High Flow Rates

The results of pulsed-flow leach tests carried out on SRL TDS-131 glass at 70°C

FIGURE 1.11. Dependence of Leachate Concentrations on Total Exposure Time in a Constant-Flow-Rate Leach Test

FIGURE 1.12. Dependence of Stabilized Leachate Concentrations on Flow Rate in a Flow Test

using deionized water as the leachant are summarized in Table 1.4 and Figures 1.15 and 1.16. The normalized concentrations and normalized leach rates which appear in these figures have been obtained by dividing the experimentally measured concentrations and leach rates of each glass component, respectively, by its weight fraction in the bulk glass composition according to Table 1.1.

FIGURE 1.13. Dependence of Leach Rates on Flow Rate in a Flow Test

The results obtained at high and moderate flow rates (above 1 m/yr) show corrosion to be the most important mechanism. The leachate concentrations observed in the flow tests steadily rise with time (see Table 1.4 and Figure 1.15) until they level off at values which are inversely proportional to the flow rate, indicating that the release rates of various glass components are independent of flow rate (see Figure 1.16). Moreover, at high flow rates the leach rates of Si and Al are nearly equal to those of B, Na, Li and Cs (the leach rates of Li at high flow rates are equal within experimental error to those of Na). This indicates that the surface layer is depleted with respect to all these elements and that a dealcalized silica-rich protective layer is not built up. Insoluble minor species such as Fe, Mn and Ni remain in the surface region, as indicated by the fact that over the entire flow rate region

Dynamic Leach Tests

Normalized Leachate Concentrations or Leach Rates

FIGURE 1.14. Relative Leach Rates of Various Glass Components in a Flow Test

TABLE 1.4. Dynamic Leach Tests on SRL TDS-131 in Deionized Water, 70°C

S/V, m ⁻¹	T _r , days	pH	Steady-State Concentration, mg/L							
			Si	B	Al	Na	Ca	Sr	Cs	Li
13 ^(a)	4.0	5.8	6.34	0.686	--	3.07	0.761	--	--	--
2.4	28	8.95	4.31	0.715	0.36	2.05	0.054	0.09	0.23	0.37
24	8	9.5	12.5	2.37	0.58	6.70	0.21	0.24	0.37	1.36
23 ^(b)	28	9.7	18.1	3.80	1.31	10.5	0.022	0.024	0.96	1.92
24	28	9.6	20.3	4.16	0.67	11.7	0.08	0.08	0.71	2.40
301	4	9.75	16.0	3.45	1.23	10.5	0.015	0.031	0.59	1.77
306 ^(b)	4	10.0	29.8	7.15	2.04	25.5	<0.01	<0.01	1.08	3.70
825	2	9.8	24.2	6.80	--	19.0	<0.1	0.02	0.80	3.54
25 ^(b)	112	10.38	55.2	22.82	0.82	53.1	<0.01	<0.01	0.90	10.6
141	28	10.80	73.2	35.17	0.36	73.8	0.001	0.004	1.13	16.7
825	8	10.7	112	52.7	0.56	122	<0.1	<0.002	1.6	26.1
301	28	10.62	103	44.5	1.42	85.1	<0.01	<0.02	1.8	18.2
306 ^(b)	28	10.85	156	79.3	1.15	156	<0.01	<0.02	2.5	32.8
825	28	11.1	232	142	0.56	347	<0.1	<0.02	3.2	69.5
301	112	11.03	138	76.3	1.10	160	0.001	0.004	2.38	34.4
306 ^(b)	112	11.24	199	118	0.96	248	0.014	0.012	3.46	52.1
970	112	11.22	214	139	1.52	337	0.014	0.021	5.40	54.3
1940	112	11.29	227	156	1.49	383	0.029	0.036	5.90	61.1
970	224	11.27	225	155	1.49	364	0.025	0.030	5.95	60.5
1940	224	11.40	269	211	1.28	483	0.058	0.078	8.15	81.0

(a) Frequent-exchange test (all others are pulsed flow tests).

(b) Monolithic sample (all other flow tests carried out on powders).

between 200 and 0.3 m/yr the observed concentration of these three elements in the leachate are <0.1 mg/L and their normalized leach rates are $<1 \times 10^{-3} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, i.e., smaller by a factor of more than 200 than the normalized leach rates of boron. In general, cations with higher charge densities (charge-to-size ratios) show an increasingly large tendency towards reprecipitation and resorption in the surface regions of leached glasses (Barkatt, Simmons and Macedo 1981). However the layer consisting only of these species is not sufficiently dense to serve as an effective protective barrier. Alternatively, a dealkalinized layer may be formed, but its stability is so low that it is ruptured before it can attain appreciable thickness and protective ability; this process, repeated at short intervals throughout the expo-

sure period, has the same consequences as simple matrix corrosion. Measurements of the structure of the surface of TDS-131 glass leached under high flow rate conditions by means of gradual etching with HF (Barkatt et al. 1984b) show that selective dealkalinization is limited to an extremely thin region (probably <0.1 μm) compared with the thickness from which both alkalis and Si have already dissolved away (see Wicks et al. 1982; Sales, Petek and Boatner 1983; and Chapter 2). This behavior is contrary to that of PNL 76-68 glass, which exhibits a thick, stable dealkalinized layer (Barkatt et al. 1984b). The results given in Table 1.4 also demonstrate that the stabilized leachate concentrations obtained with different combinations of S/V and T_r follow the same general pattern of dependence on the product T_r·(S/V), and that results obtained in powder tests at

FIGURE 1.15. Results of Dynamic Leach Tests on SRL TDS-131, Deionized Water, 70°C, Normalized Concentration Versus $T_r \cdot (S/V)$

FIGURE 1.16. Results of Dynamic Leach Tests on SRL TDS-131, Deionized Water, 70°C, Leach Rate Versus Contact Time (equivalent flow rate)

various contact times are in good agreement with those obtained in tests on monolithic samples (cf. 1.3.5 and 1.3.6).

(b) Low Flow Rates

Comparison of the findings discussed so far at high flow rates with the results of experiments carried out at lower flow rates shows that in the slow-flow region the character of the leaching process undergoes a fundamental change. Figure 1.16, which summarizes the data obtained at 70°C, shows that at contact times longer than 200 days (with S/V ratios normalized to a value of 60 m^{-1} , corresponding to flow rates slower than 1 m/yr, Barkatt et al. 1983a) the steady-state leachate concentrations obtained in flow tests become nearly independent of flow rate and stabilize at the values shown in the last four lines of Table 1.4. Since leachate concentrations become nearly constant, the resulting normalized leach rates fall off from a value of approximately $0.3 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ at high flow rates to less than $0.005 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ below 10^{-2} m/yr (see Figure 1.16). [The latter normalized leach rate corresponds to a fractional loss rate of $1 \times 10^{-5} \text{ yr}^{-1}$ under typical repository conditions (Barkatt et al. 1983a)]. The small residual rise in silica levels at lower flow rates can be fully attributed to the corresponding increase in leachate pH, based on the pH dependence of SiO_2 solubility (Alexander, Heston and Iler 1954). At slow flow rates the leach rates of Al are extremely small, and those of Si are only one-fifth of the leach rates of Na, Li and B. This implies that the surfaces which develop under slow-flow conditions are substantially more enriched with respect to Si and Al than those which are formed at high flow rates. (Minor insoluble species such as Fe, Mn and Ni remain in the layer even at high flow rates.) It is interesting to note that in the region of very slow flow rates even the leach rates of Li and Na become significantly lower than that of B (The normalized leach rates of Li are generally close to those of Na at all flow rates, while the normalized leach rates of Cs are close to those of Si.) The transition from nearly congruent dissolution with respect to B, Na, Li, Si, Cs and Al at high flow rates to selective leaching of the first elements of this series at slow flow rates is in all cases smooth and gradual, indicating that the appearance of alteration products is not a rapid, abrupt change.

Material balance calculations based on comparison of leachate concentrations in the slow-flow region with the composition of the bulk glass (see Table 1.1) indicate that the most abundant components left behind in the leached surface are present at relative concentration ratios corresponding to the compositions of silica-rich, alkali-containing species such as acmite (aegirine), $\text{NaFeSi}_2\text{O}_6$ (see Wicks et al. 1982) and analcime $[\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}]$ (see Bates and Steindler 1983 and Section 1.5.9 and Chapter 2 below)].

One of the most prominent features of the results of the tests on SRL TDS-131 glass is the large extent of the pH excursion. When the flow rate is decreased from 194 m/yr to 0.57 m/yr, the final pH readings rise from 8.95 to 11.1 (Barkatt et al. 1983a). At slower flow rates of 0.121, 0.061 and 0.031 m/yr the corresponding pH readings continue to rise to 11.22, 11.28 and 11.40, respectively (Table 1.4). In a 1-yr fine powder solubility test in tightly sealed vessels the pH value was found to reach 12.4 (cf. 1.5.4). It is the prolonged, extensive pH rise which causes high-flow, unsaturated leach behavior to extend in the case of SRL TDS-131 glass all the way down to flow rates of about 1 m/yr. [The linear interstitial flow rate used here is directly proportional to the volumetric flow rate and inversely proportional to the cross-section of the canister and to the rock porosity (Barkatt et al. 1983a). For instance, in the case of a canister with a diameter of 0.6 m and a length of 3 m and a rock porosity of 0.16 (Barkatt et al. 1983a) a linear flow rate of 1 m/yr at a direction perpendicular to the long axis of the canister corresponds to a volumetric flow rate of $0.28 \text{ m}^3/\text{yr}$ or 32 mL/hr .] In the cases of less alkaline glasses, saturation is expected to appear at much higher flow rates, but in the present case the exponential dependence of silica (Alexander, Heston and Iler 1954) and alumina (Dezelic, Bilinski and Wolf 1971) solubility on pH prevents the increasingly concentrated leachates at slow flow rates from approaching the saturation limit. At a flow rate of 0.031 m/yr, for instance, the observed concentration of dissolved Si at 70°C is 269 mg/L. In the solubility experiment mentioned above the Si level is 1750 mg/L. These values are much lower (at least by a factor of 20 based on Alexander, Heston and Iler 1954; Morey, Fournier and Rowe 1964) than the solubility of silica at the observed pH values, indicating that they are determined by the solubilities of more stable surface alteration products such as the

aluminosilicates and iron silicates mentioned above, resulting in a significant retardation of material loss rates under slow-flow conditions. At the same time, Si concentrations are considerably higher than the solubility of silica at 70°C in neutral environments, which is 113 mg/L Si (Alexander, Heston and Iler 1954; Morey, Fournier and Rowe 1964). Accordingly, recent models which use the solubility of amorphous silica in neutral media as the basis for calculation of upper limits on long-term leach rates of nuclear waste glasses (Barkatt et al. 1982; Chambre, Pigford and Zavoshy 1982) have to be modified to take the pH excursion into account. Long-term limiting pH levels should be evaluated and the corresponding solubilities of the major glass components (which steeply increase with rising pH in the cases of SiO_2 and Al_2O_3) should be calculated and used to predict upper limits for the dissolution rates.

As detailed above, the results of the flow tests can also serve to distinguish between leach behavior controlled by diffusion on one hand and by corrosion on the other when leachate concentrations are monitored as a function of time in an experiment carried out at a given flow rate. The data shown in Figure 1.17 were obtained in an experiment carried out on a freshly cut sample which was exposed under conditions of $S/V = 24.8 \text{ m}^{-1}$ and a residence time T_r of 28 days (25% exchange every 7 days), corresponding to a flow rate of 18.9 m/yr (Barkatt et al. 1983a). At the end of 161 days T_r was increased to 112 days, corresponding to a flow rate of 4.7 m/yr. The leachate concentration during both parts of the experiment show a steady rise towards a constant level, in agreement with a corrosion mechanism. The experiments summarized in Figure 1.18 were carried out at higher values of S/V and T_r , corresponding to slower flow rates. It is

FIGURE 1.17. Results of Dynamic Leach Tests on SRL TDS-131, Deionized Water, 70°C, Intermediate Flow Rates, Concentration Versus Total Exposure Time

FIGURE 1.18. Results of Dynamic Leach Tests on SRL TDS-131, Deionized Water, 70°C, Slow Flow Rates, Concentration Versus Total Exposure Time

observed that in these cases the initial rise in concentration with time is followed by a decrease, which indicates reduction in leach rate due to the formation of an altered dissolution-limiting surface (cf. Figure 1.11). It should also be noted that in the two experiments conducted at $S/V = 1940 \text{ m}^{-1}$, $T_r = 112 \text{ d}$ and at $S/V = 970 \text{ m}^{-1}$, $T_r = 224 \text{ d}$, respectively, the entire concentration versus time curves are identical within experimental error, indicating that the equivalence of T_r and S/V is valid not only in the high flow rate region (Barkatt et al. 1983a) but also at slow flow rates.

It was noted that the final concentrations of each of the leached species obtained in the slow-flow experiments shown in Figure 1.18 are dependent on the flow rate only to a very small extent, indicating an approach to a leachate composition which is constant (except for a continuing dependence on pH). The Si concentration at this point is much lower than the solubility of amorphous silica at the corresponding temperature and pH (Alexander, Heston and Iler 1954; Morey, Fournier and Rowe 1964). A similar effect is observed in the case of other species, most notably Al and Cs. Accordingly, both the kinetics and the final leachate compositions indicate that at slow flow rates the dissolu-

tion becomes characterized by the formation of an altered surface layer which, upon the establishment of steady state, controls the concentrations of leached species at lower values than those expected for the unaltered glass. This is different from the classical picture of the formation of a hydrated, dealkalized but otherwise unchanged layer formed on simple silicate glasses at high dilutions. This difference is reflected in the following observations:

- (a) At high and moderate flow rates no decrease in leach rates is observed (see Figure 1.17) over time scales corresponding to those at which such a drop is observed at slow flow rates (Figure 1.18). The formation of a hydrated, dealkalized surface layer on the initially dry glass is equally probable at slow flow rates and at high flow rates. Since the decrease in leach rates is observed only at slow rates, it cannot be attributed to such an initial hydration process. There are no grounds to expect that a hydrated, dealkalized surface layer would be formed on an initially dry glass only when the flow rate is slow.
- (b) The results of the frequent-exchange test (Figure 1.3) furnish direct evidence that

the build-up of the hydrated, dealcalized surface layer is completed within the first 10 to 20 days. (A similar conclusion can be derived by comparing the flow test data in Figure 1.17 with the calculated concentration-versus-time curve at a constant leach rate (Barkatt et al. 1981). On the other hand, the decrease in leach rates in the slow-flow experiments occurs over a period of about 300 days. For such prolonged periods the rapid-flow data show that the dissolution process is linear with time (rather than parabolic) and nearly congruent.

- (c) The limiting concentration of Si in the slow-flow test is much lower than the Si concentration based on the solubility of vitreous silica at the corresponding temperature and pH level. The ultimate concentrations of alumina and of other glass components are also much lower than the solubilities of the corresponding pure oxides. Since hydration and dealcalization are not expected, by themselves, to cause changes in ultimate solubilities (see above) it is more likely that an alteration process takes place, leading to the formation of more stable, less soluble products.

It is very interesting to note that experiments at 190°C (where rapid crystallization occurs at the glass-leachate interface) directly show that uncorroded glass specimen effectively corrode in the presence of a presaturated leachate (Van Iseghem, Timmermans and de Batist 1984). This provides strong, direct evidence for the conclusion that upon prolonged contact the leachate becomes saturated with respect to more stable alteration products rather than with respect to the original glass, which has a higher solubility. Accordingly, it is concluded that the altered surface layer formed at slow flow rates has a different character than the 'classical' diffusion-limiting hydration layer and that this layer evolves subsequent to, rather than prior to, a process of linear, congruent dissolution. This altered layer can be termed 'protective' in the general sense of a surface region which limits the rate of material loss, since the alteration process is observed to result in considerable retardation of the rate of accumulation of even the most soluble glass components (boron, alkalis) in the aqueous phase. This conclusion is supported by direct observations of surface layer evolution (see Chapter 2). Formation of more stable alteration phases at long contact times can account for the apparent formation of a protective layer in cases (Scholze et al. 1982)

where the dissolution itself appears to be almost congruent.

It should be noted that the conclusions based on the results of the flow tests agree to a large extent with the major assumptions of the leaching model of Wallace and Wicks (1983). These authors concluded that the interdiffusion process attains steady state within the first few days of leaching and can be ignored when modeling for the long term; that waste glass corrosion is congruent but only a fraction of the glass components find their way into the leachate; that the remainder of these elements, including virtually all of the Fe and Mn and part of the Al and Si precipitate in the surface layer while Cs and Sr are absorbed by the insoluble compounds in the layer; and that the pH of the leachate depends on the relative amounts of leached alkali ions on one hand and of dissolved borate and silicate on the other. The reprecipitated layer, according to this model, is distinct from the initially formed gel layer. Unlike the gel layer, which does not control the leaching kinetics in the long term, it contains considerable amounts of water so that silica can continue to dissolve from the gel layer but in order to get into the leachate it must now diffuse through the precipitated layer. The experiments described above confirm the basic assumptions of the model. A more detailed discussion of the Wallace-Wicks model is given in Chapter 6.

The Wallace-Wicks model describes the formation of a dissolution-limiting reprecipitated layer, but it does not address the question of the possible effects on the release kinetics which would be observed if the thickness of the layer eventually reaches a steady state instead of continuing to grow indefinitely. The experiments described in the present section indicate that the dissolution-limiting layer (unlike the gel layer formed under rapid-flow conditions) contains a large fraction of silica. The solubility of the silica alteration products [which may include quartz, cristobalite, hydrated silica (Spychalski 1938), alumino- and ferrosilicates], although lower than that of amorphous silica, is significant. The same is true, for instance, in the case of the alumina alteration products (most probably aluminosilicates). Accordingly, the concentrations of the major matrix elements, in particular silica, under slow-flow conditions, are expected to level off at values corresponding to the solubilities of the alteration products. This expectation is fully borne out by the Si data in Figure 1.18. When saturation has been reached, further dissolution of silica

from the glass only takes place to an extent which balances the loss of silica due to flow of solution out of the system according to eq. (1.9).

The observation that the normalized concentrations of the highly soluble components of the glass - Na, Li and B - in the leachate rise to levels which are approximately 4 times higher than that of Si at long contact time (Figure 1.16) is in complete agreement with the hypothesis of the build-up of a silica-rich alteration or reprecipitation layer which is depleted with respect to the soluble glass components. Under the slow-flow conditions discussed here, Si and Al apparently dissolve at the same rate as B, Na and Li, as in the rapid-flow case, but at long contact times, most of the Al and Si redeposit in the alteration layer and in the gel layer, resulting in lower relative concentrations of these elements in the solution. However, the observation that the concentrations of these species monitored as a function of time closely follow the concentration-time curve observed in the case of Si cannot be easily explained in terms of solubility alone. Mass balance calculations show that even at the slowest flow rates covered in Figure 1.16 only a small fraction of the Na and Li remains in the surface layer. Large-scale retention of these elements, probably as alkali aluminosilicates, only takes place at much longer contact time and higher pH values (see 1.5.4). In the case of boron, no retention in the surface layer is indicated by mass balance calculations or by direct spectroscopic techniques (see Wicks et al. 1982; Bates and Steindler 1983; Wallace and Wicks 1983; and Chapter 2) and no likely low-solubility products have been identified.

It can be concluded that the alteration layer acts as an effective barrier, preventing the alkalis and boron present in the glass from reaching the aqueous solution. However, the results described above cannot be easily explained by use of the "classical" model of layer growth, which assumes that (i) the layer build-up consists of the selective leaching of soluble species, mainly alkalis; (ii) this selective leaching is diffusion-controlled and characterized by a constant diffusion coefficient resulting in increasingly slower but ever-continuing layer growth. If this picture was valid, the concentrations of B, Na and Li should have decreased with time more gradually than the concentration of Si, and continued to drop with time after the concentration of Si has reached a constant level (as in the lowest curve in Figure 1.11). Instead, the concen-

trations of B, Na and Li follow very similar kinetic patterns to that of the Si concentration, and these concentrations appear to level off at values which are approximately 4 times higher than that of the concentration of Si on a normalized basis (see above). This behavior can be explained by the following assumptions:

- (a) The alteration layer can only reach a certain maximum thickness, due either to (i) stress-induced separation beyond a certain critical thickness or (ii) inability of glass layers covered by a layer of alteration products to rearrange and further increase the depth of the altered layer.
- (b) B, Na and Li present in the glass covered by the fully developed alteration layer exhibit virtually complete inability to migrate through the layer. Accordingly, further leaching of B, Na and Li follows the dissolution of Si which compensates for the loss of Si from the aqueous phase due to the effect of flow.

This set of assumptions can be viewed as a sorbed reaction product model (Kuhn and Peters 1982) rather than as a classical layer build-up model. Alternatively, assumptions a(ii) and b are equivalent to postulating that the diffusion coefficient is not constant across the layer, but rapidly increases upon going from the outer edge of the protective layer towards the unaltered glass. This assumption has been recognized as more realistic than the picture of a constant diffusion coefficient (Holland 1966; Douglas and El-Shamy 1967) and has been confirmed by observations on silicate glass resistivity (Johansson, Karlberg and Wickby 1975).

It can be concluded that a model based on the build-up of an alteration layer of a finite thickness which is a very effective barrier against migration of all glass components is compatible with the experimental findings summarized above. It should be emphasized that this rate-controlling layer is quite distinct from the porous gel layer which continues to grow as the unaltered glass recedes due to the effect of flow (see above) and more insoluble glass components (e.g., oxides of Fe, Mn and Ni) are released from the glass matrix but remain precipitated on the surface.

The assumption that the long-term release rates of soluble species are controlled by protective surface layers has been supported by direct observations in the long-term burial experiment at Chalk River (Walton and

Merriitt 1980), which indicated that the leach rates of Sr and Cs exhibit a dramatic increase when a small section of the total surface of the glass is disturbed. The Chalk River experiment has been conducted under conditions which are significantly different from those of the geologic disposal of defense waste glass both with respect to glass composition (nepheline) and to burial conditions (shallow burial in wet ground, no engineered barriers). Nevertheless, this experiment indicates that under certain conditions surface films formed around the bulk glass can limit the long-term release of soluble species.

1.4.4 Static Tests

MCC-1 leach data at 90°C show that initially the kinetic behavior of TDS-131 glass dissolution follows a t^{α} rate law where α lies between 0.25 and 0.5 (Wallace and Wicks 1983). However, it is difficult to obtain a fit with a simple diffusion model, and it is concluded that a very rapid leaching process takes place within the first few hours or days, and that its extent seems to vary from sample to sample and may be related to the nature of the initial surface (Wallace and Wicks 1983). If the pH is deliberately buffered at a value between 7 and 8.5 (Plodinec, Wicks and Bibler 1982; Wallace and Wicks 1983; Wicks, O'Rourke and Whitkop 1982) a precipitated surface layer is subsequently formed and controls the leach kinetics over the next 6 months (Wicks et al. 1982; Wallace and Wicks 1983). This conclusion is based, in addition to the kinetic evidence, on the results of surface analysis and on the observation that when the leachate is buffered at pH 3 the leaching is completely congruent and no reprecipitated layer is detected (Wallace and Wicks 1983; Wicks, O'Rourke and Whitkop 1982). However, when the pH is not buffered at a near-neutral level, alkali leaching from the glass rapidly causes a rise beyond this value to final values as high as 11.7 (Wicks et al. 1982) (depending on the S/V ratio) and the controlling mechanism is network dissolution. Experiments carried out at higher S/V ratios show quicker saturation of the leachate with respect to silica, iron, and other insoluble species, and the precipitation of alteration products such as acmite on the leached surface (Wicks et al. 1982). Longer-term MCC-1 tests on TDS-131 glass show that a simple corrosion behavior (linear rate law) persists for the first 30 days, but when the tests are carried out for periods of 200 to 400 days the leachate composition stabilizes at values (Bates, Lam and Steindler 1983) which correspond to a pH of 10.6. The results of dynamic tests (Barkatt et al. 1983a)

at such a pH value, adjusted for the S/V ratio (10 m^{-1}) and temperature (90°C) used in the static tests are in reasonable agreement with the results of the static tests. However, a much better comparison between the two types of test is available in the case of Defense Waste Reference glass (see 1.5.8), where the same S/V ratio and temperature were used in the two tests.

1.4.5 High-Temperature Tests

High-temperature studies on SRL TDS-131 glass between 120 and 240°C (Bates and Steindler 1983) show that the attack of water on the glass proceeds by two mechanisms. When the hydration layer thickness is plotted against $t^{1/2}$, where t is the exposure time, a line with a constant slope is obtained. After a certain period of time the slope suddenly changes and the subsequent rate of hydration is much faster. This period of time is shorter at higher temperatures and it also depends on glass composition. The change in the kinetics indicates a change in the nature of the products of the alteration of the hydrated layer. Apparently the first mechanism involves the formation of analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), a calcium-free crystalline phase (see Chapter 2), while calcium accumulates in the surface layer closest to the original glass. When the second mechanism takes over, tobermorite ($\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$) is formed and rapidly depletes the calcium from the outer layers of the glass. It is obvious that the total extent of attack on the glass at the end of an arbitrary period of time cannot be expected to yield a simple Arrhenius-type temperature dependence, since the changeover between the two mechanisms which are involved in the process is also temperature-dependent. However, when only one of the mechanisms is considered, linear Arrhenius plots are obtained (Bates and Steindler 1983) indicating the need to consider temperature effects at the same stage of the reaction rather than at a common arbitrary time (cf. 1.3.9 and 1.4.6). The major crystalline alteration product identified is analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$). This composition agrees well with conclusions concerning surface composition based on flow test data at 70 to 90°C (see 1.4.3 and 1.5.9). At higher temperatures and longer times the formation of tobermorite, $\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$, is also observed. The results demonstrate that carefully analyzed high-temperature data can be very valuable in developing long-term predictions for the progress of corrosion processes at low temperatures. A more comprehensive study of high-temperature behavior was carried out in the case of the Defense Waste Reference Glass

(1.5.7). In the case of TDS-131, extrapolation of preliminary data obtained between 170 and 225°C indicates that the times required for the appearance of visible amounts of crystals on the glass surface are approximately 4 years and 20 years at temperatures of 90 and 70°C, respectively. These times (which are at present uncertain within a factor of 3), are somewhat longer than the period required for leachate concentrations to level off after dropping from their maximum values. As shown in Figure 1.18, the latter time is about 1 year at 70°C. (It should be noted that the kinetic experiments at 70°C and the high-temperature experiments were conducted at similar values of S/V.) This result can be readily interpreted by assuming that the extent of reprecipitation and alteration required to form a layer which controls the composition of the solution with which it is in contact is much smaller than the extent of alteration necessary to produce significant amounts of large, visually observable crystals on the glass surface.

The formation of the initial set of alteration products does not conclude the series of chemical transformations which take place upon very prolonged exposure. In the specific case discussed here, analcime is a "first-generation" alteration product while tobermorite appears at a later stage. More generally, solution concentrations and material release rates at long times are likely to be determined by saturation with respect to a series of solid phase assemblages, each closer to thermodynamic stability than its predecessors, which transform into each other under steady-state conditions. (In the case of highly soluble species, the material transport properties across these solid phases may also be important, as detailed in Section 1.4.3.2.) This is true both for a glass-water system and for a more complex glass-barrier-rock-water system. A comprehensive discussion of these long-term phenomena has been given by Apted (1982). Eventually, such successive solid-state transformations are expected to control dissolution behavior under very slow flow conditions even at low temperatures (40 to 90°C), although transformation rates will be much slower than under hydrothermal conditions.

1.4.6 Temperature Effects

In addition to the mechanism diagnostic features of isothermal leach tests discussed above (see 1.4.3.2), the comparison of data obtained at several different temperatures can be useful in determining leach mechanisms. As noted above (1.3.9), it is necessary to ensure that measurements at the vari-

ous temperatures employed apply to the same process (e.g., matrix corrosion, saturation, or alteration and formation of a particular type of alteration product); i.e., that all of them reflect the same controlling mechanism.

Both diffusion-controlled dealcalization and matrix corrosion generally follow an Arrhenius-type dependence, i.e.,

$$k = A \exp(-E_a/RT) \quad (1.12)$$

where k is the rate of reaction, E_a is the activation energy, R is the gas constant, T is the temperature in degrees kelvin and A is a constant. The values of E_a generally range around 80 to 100 kJ (Lyle 1943; Rana and Douglas 1961; Holland 1966). Corrosion of the silicate matrix in water or in alkaline media is generally characterized by slightly lower activation energies, usually around 60 to 80 kJ. This applies to simple silicate glasses (Rana and Douglas 1961; Holland 1966; Hubbard and Hamilton 1941) as well as to natural glasses (Barkatt et al. 1984a), aluminosilicate minerals such as nepheline (Tole 1982) and commercial nuclear waste glasses (Barkatt, Simmons and Macedo 1981).

Material loss under slow-flow conditions, on the other hand, is solubility controlled. The solubilities S are determined by exponential expressions of the type (Morey, Fournier and Rowe 1964)

$$S = S_0 \exp(\Delta H/RT) \quad (1.13)$$

where S_0 is the solubility at a reference temperature and ΔH is the enthalpy of dissolution. Since $\Delta H < 0$, eq. (1.13) resembles eq. (1.12), both expressing exponential dependence on temperature. However, in the case of siliceous materials $-\Delta H$ is much smaller than the values of E_a given above, amounting in the case of amorphous silica only to 14 kJ (Morey, Fournier and Rowe 1964) and to even smaller values in the cases of certain aluminosilicates (Tole 1982; Barkatt et al. 1982).

In the case of SRL TDS-131 defense waste glass, short-contact-time (modified IAEA) tests were carried out in deionized water at various temperatures until the leach rates were observed to approach stabilization. The results are given in Table 1.5 and in Figure 1.19. The data agree with an activation energy of (100 ± 13) kJ. These results represent the limiting nonsaturating case, and they agree with previously observed activation energies for silicate glasses (Rana and Douglas 1961; Holland 1966).

TABLE 1.5. High Dilution Tests at Various Temperatures, SRL TDS-131 Glass, Normalized Leach Rates, $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$

Temperature, °C	Duration, Days	Si	Cs	Sr	Al	Na	B
120	5.5	3.1	3.7	2.1	2.2	4.7	4.2
90	15	0.70	0.89	0.71	0.55	1.1	0.97
70	22	0.25	0.17	0.24	0.34		
40	62	0.0045	0.025	0.0081	0.0022	0.010	0.010
23	62	0.0009				0.0028	0.0010

FIGURE 1.19. Results of Frequent-Exchange Tests on SRL TDS-131 in Deionized Water at Various Temperatures

Static tests (Plodinec, Wicks and Bibler 1982) carried out both in deionized water and in ground water gave results which correspond to a temperature-dependence parameter of (56 ± 6) kJ between 40°C and 90°C but only (32 ± 3) kJ between 90°C and 150°C. The final silica concentrations in the test (a 28-day MCC-1 or MCC-2 test, $S/V = 10 \text{ m}^{-1}$) were 6.1, 118 and 526 mg/L at 40, 90 and 150°C, respectively. At the higher temperatures these values approach the solubility of silica (based on Alexander, Heston and Iler 1954; Morey, Fournier and Rowe 1964), since

the enthalpy of dissolution of amorphous silica [about 14 kJ (Alexander, Heston and Iler 1954)] is much lower than the activation energy of leaching in unsaturated media (about 80 kJ, see above). This supports the conclusion (1.3.9) that in order to characterize the temperature-dependence it is necessary to compare data obtained for the same chemical stage of the glass/water interaction rather than for the same total duration of the exposure (see Section 1.3.9). In agreement with these observations, a single dynamic test carried out at an intermediate flow rate ($S/V = 825 \text{ m}^{-1}$, $T_r = 28$ days) also indicated that the temperature-dependence parameter is <66 kJ, i.e., an intermediate value between the activation energy for leaching at high dilution and the enthalpy of solution under conditions of saturation or very slow flow. More extensive temperature data are shown in 1.5.6 below.

1.4.7 Tests in Silicate Ground Water

The effects of environmental interactions will be discussed in detail in Chapter 3. A brief mention is made in the present section of those findings which directly relate to the general mechanisms of the dissolution of the glass matrix.

The principal factors involved in the effect of leachant composition on corrosion rates are pH and presence of saturating species, e.g., Si and Al. However, another effect which has to be considered is a possible increase in leachability of particular glass components, e.g., transition metals, lanthanides and actinides, due to the presence of complexing species, e.g., chloride, fluoride, sulfate, carbonate and bicarbonate in ground water.

Static MCC-1 tests on SRL TDS-131 in MCC silicate water (Materials Characterization Center 1981) have shown that the dissolution rate of Si in this leachant, which contains 27 mg/L Si and has a pH of 7.5, is lower by

about 40% than in deionized water (Plodinec, Wicks and Bibler 1982). Retardation of dissolution rates is also observed in simulated basalt, granite, shale and tuff ground water (Plodinec, Wicks and Bibler 1982; Wicks, Robnett and Rankin 1982). The leach rates of B and Cs are also depressed in ground water (Plodinec, Wicks and Bibler 1982), but those of U and Fe are enhanced (Plodinec, Wicks and Bibler 1982; Stone 1982), and the leach rate of U becomes similar to the matrix dissolution rate based on Si, while in deionized water the leach rate of U is much lower.

1.5. EFFECTS OF GLASS COMPOSITION: MCC DEFENSE WASTE REFERENCE GLASS AND COMPARISON WITH SRL TDS-131

SYNOPSIS

The composition of the glass is a major factor in determining the controlling mechanisms of glass dissolution throughout the period during which the glass is exposed to water. The effects of composition, however, strongly depend on the contact time between the glass and the water around it.

The difference in chemical composition between SRL TDS-131 glass (44% SiO_2 , 13% Na_2O) and DWRG (50% SiO_2 , 8% Na_2O) is not very large. At short contact times the leach rates of TDS-131 are higher only by a factor of 1.5 to 2 than those of DWRG. However, at long contact times (slow flow and large S/V ratios), when solubilities dominate the extent of material loss, TDS-131 exhibits loss rates higher by 2 orders of magnitude and pH levels higher by 2 units than the corresponding values obtained for DWRG. For instance, in a 1-year experiment at a high S/V ratio at 70°C TDS-131 powder loses 93% of its boron content and 3.2% of its silicon content and the pH is 12.4, while in a parallel experiment on DWRG the losses of B and Si only amount to 0.8% and 0.2%, respectively, and the pH is 10.7. The slightly higher alkali content of TDS-131 glass is concluded to give rise to an increase in leachate alkalinity which is sufficiently large to cause a dramatic increase in the solubility and material loss from the glass.

The relatively small pH excursion in the case of DWRG causes steady-state DWRG leachates obtained under flow conditions to reach the constant-composition region at relatively high flow rates. This implies that under repository conditions an increase in glass surface area, e.g., as a result of fracture, will not lead to significant changes in leachate composition and in material loss rates.

1.5.1 General

This section consists of a comparative description of the mechanisms which control the leaching of two defense waste forms, viz. SRL TDS-131 glass (see 1.4) and MCC DWRG. It is shown that both the leach mechanisms and the structure of the leached surface are strongly dependent not only on the composition of the leachant and the contact time between the leachant and the glass but also on the exact composition of the glass. The relatively minor differences in composition between the two glasses investigated here were observed to give rise to rather large differences in leach kinetics, especially in the case of prolonged contact with water.

As shown in Table 1.1, the two glasses discussed in this section do not appear very different; DWRG contains (on a relative basis) about 40% less Na_2O , 30% less Fe_2O_3 and 25% less B_2O_3 and MnO_2 than SRL TDS-131, and on the other hand it has about 15% more SiO_2 and 40% more Al_2O_3 , as well as an appreciable quantity of U_3O_8 .

1.5.2 Short-Contact-Time Tests

At high flow rates or high dilutions, corresponding to short contact times between the glass and the surrounding water (so that there is little effect of glass dissolution products on the composition and reactivity of the solution), the leach behavior of the two glasses is not very different. A modified IAEA (Hespe 1971) frequent-exchange test at 90°C on polished rectangular samples using deionized water as the leachant shows that at the end of 30, 120 or 360 days the leach rates of DWRG are lower by a factor of about 1.5 than the leach rates of TDS-131 (see Table 1.6). These results agree with findings concerning the relative durabilities of SRL glasses TDS-131 and TDS-165 (the latter is generically similar to DWRG) in short-term (3-day) tests carried out in neutral solutions (Soper et al. 1983).

1.5.3 Flow Tests

1.5.3.1. Continuous-Flow Tests

Leaching experiments have been performed on DWRG by Clark and coworkers at the University of Florida using the partially CO_2 -buffered, rapid rate, continuous flow test method described in 1.3.4.2 and 1.4.3.1. The concentrations of Si and Na are shown in Figure 1.20 for up to 140 days of leaching at a flow rate of 0.1 mL/hr and $\text{S/V} = 10 \text{ m}^{-1}$. The same general trends are observed for this glass as for the SRL TDS-131 glass. There is an

TABLE 1.6. Comparison Between TDS-131 and DWRG Leach Data in Deionized Water, Modified IAEA, 90°C

	Leach Rates, $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$			
	TDS-131		DWRG	
	30 d	360 d	30 d	360 d
Si	0.82	0.53	0.67	0.25
B	1.09	0.70	0.73	0.34
Na	1.14	0.75	0.80	0.47
Li	n.d.	n.d.	0.81	0.37
Cs	1.02	0.48	0.86	0.40
Sr	0.079	0.057	0.38	0.072
Ca	0.084	0.079	0.33	0.092
Al	0.73	0.41	0.60	0.21
Fe	<0.001	0.001	<0.002	<0.001
U	n.p.	n.p.	0.040	0.032

n.d. = not determined

n.p. = not present in specimen.

FIGURE 1.20. Concentrations of Si and Na Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on TDS-131 Glass

initial increase in the solution concentrations with time up to about 28 days of exposure and then a slight decrease until about 56 days at which time steady state appears to have been established. A similar trend is also observed for the solution pH in Figure 1.21. The major differences between DWRG and TDS-131 glass are the absolute concentrations and pH. These values are much

FIGURE 1.21. Leachate pH Values Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on DWRG

smaller in the case of DWRG, indicating a smaller release rate (compare Figures 1.4 and 1.20, and Figures 1.6 and 1.21). Figures 1.6 and 1.21 indicate that about 3 months are required to produce the same weight loss on DWRG as for TDS-131 after 1 month under equivalent conditions of flow. The Si and Na release rates are also plotted on Figure 1.5 for the purpose of comparison. Normalized total mass losses for DWRG under flow conditions in deionized water are plotted as a function of corrosion time in Figure 1.22. DWRG is generally more durable than TDS-131 glass. It appears that higher flow rates are required to enter Region 2 and that the maximum release rates are smaller in the case of DWRG as indicated in Figure 1.5. Additional discussion of DWRG leaching under flow conditions in the presence of various leachants and waste package materials is presented in Chapter 3.

1.5.3.2 Pulsed-Flow Tests

The partial-exchange dynamic test described above (1.3.4.2, 1.4.3.2) permits investigating the effects of flow over a wide range of contact times (or flow rates). Representative results of this test carried out at 70°C on polished rectangular samples at several flow rates, using both deionized water and simulated Grande Ronde basaltic ground water (Wood and Salter 1980; Jones 1982) as leachants, are given in Table 1.7. (Tests carried out in the additional presence of 304L stainless steel with one-third the surface area of the glass in ground water showed no significant effect of the steel on the results, Chapter 3.) The data show that under flow

FIGURE 1.22. Normalized Total Mass Loss Measured as a Function of Corrosion Time in Continuous-Flow Leach Tests on DWRG

TABLE 1.7. Effects of Glass and Leachant Compositions on the Results of Flow Tests at 70°C

	SRL TDS-131			MCC DWRG		
	DI Water	DI Water	DI Water	DI Water	Ground Water	Ground Water
Flow rate, m/yr	10.7	1.99	10.8	2.42	12.2	1.75
pH	10.0	10.7	9.65	9.70	9.57	9.53
	Normalized Leach Rate $\times 10^2$, $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$					
Si	10.5	7.1	6.17	1.85	0.80	0.12
B	17.5	23.2	8.78	2.53	1.64	0.26
Na	21.9	18.7	7.84	2.50		
Cs	12.5	6.9	9.32	3.09	2.44	0.34
Li	16.4	21.4	9.37	2.50	2.37	0.39
Ca	<0.1	<0.2	2.35	0.24		
Sr	0.1	<0.1	0.35	0.13	1.39	0.36
Al	6.7	0.3	5.55	1.45	0.65	0.18
Fe	0.06	0.11	0.02	0.10	0.10	0.005
Cr				0.36	<0.01	<0.01
Mg				<0.01	<0.01	<0.01
U			0.92	0.67	1.05	0.25

conditions equivalent to a relatively high flow rate of about 11 m/yr the leach rates obtained with DWRG are lower only by 40% than those obtained with SRL TDS-131 glass, in agreement with the IAEA test results. However, when the flow rates are reduced to about 2 m/yr the leach rates of the major components of SRL TDS-131 glass decrease only by 15 to 20%, while those of MCC Defense Waste Reference Glass (DWRG) drop by a factor of 3 to 3.5. In other words, the leachate concentrations in the case of DWRG approach saturation at much shorter contact times than those at which saturation is observed in the case of SRL TDS-131 glass. The results in the case of leaching DWRG in ground water are indicative of complete saturation, since a decrease by a factor of 7 in flow rate leads to a corresponding decrease in the leach rate, as shown in Table 1.7. As explained below, this is also evident upon monitoring the leachate concentration as a function of time during the flow test, as shown in Figure 1.23. (Note that each of the pulsed-flow

FIGURE 1.23. Results of Dynamic Leach Tests on DWRG, Ground Water, 70°C, Intermediate Flow Rates, Concentration Versus Total Exposure Time

experiments reported in the present chapter was performed at least in duplicate. The readings obtained in individual flow tests are shown, for instance, in Figures 1.18, 1.23, 1.24, 1.25. The separations between data points corresponding to the same exposure time represent the differences between the tests carried out in multiplicate. Analytical accuracy in the determination of the major glass components in solution was generally within $\pm 10\%$ as shown both by intra-laboratory repeated determinations and by analysis of representative leachates at The Catholic University of America and, in parallel, at the University of Florida. In

FIGURE 1.24. Results of Dynamic Leach Tests on DWRG, Deionized Water, 70°C, Intermediate Flow Rates, Concentration Versus Total Exposure Time

FIGURE 1.25. Results of Dynamic Leach Tests on DWRG, Deionized Water, 70°C, Slow Flow Rates, Concentration Versus Total Exposure Time

addition, blank tests were carried out under the same conditions as the tests on the actual glass samples.)

Another indication of the difference between the behavior of the two glasses at low flow rates is provided by monitoring the leachate concentrations as a function of time. As previously discussed (1.4.3.2), when in the course of a flow test the leachate concentrations are observed to rise steadily with time until they level off at a constant value, this indicates that the leaching process is controlled by a simple corrosion mechanism and that the surface layer is not protective. On the other hand, when the leachant concentrations rise to maximum values and then decrease again, reflecting a decrease in leach rates, before a steady state is achieved, one can infer the presence of a surface layer which acts as a protective barrier. In the case of leaching tests on SRL TDS-131 glass

in deionized water at 70°C, the second type of behavior only appears at flow rates of 0.12 m/yr or slower (1.4.3.2). Upon plotting leachate concentrations as a function of time in corresponding tests on DWRG the resulting plots do not exhibit a maximum when the flow rate is 10.8 m/yr (see Figure 1.24), and apparently not even when it is only 2.42 m/yr (see Figure 1.25). (Measurements at slower flow rates are still in progress at the time of writing.) However, at flow rates below 2 m/yr the normalized dissolution rate based on Si clearly becomes much slower than those of the alkalis and boron, as a stable silica-rich (and alumina-rich) leached layer is formed. As emphasized above, the experimental data can be interpreted by assuming that this layer is protective in the sense that it imposes lower solubilities on the major matrix elements of the glass (in particular Si) due to the formation of alteration products, and the resulting alteration layer is a very effective barrier, retarding the dissolution of even the most soluble components of the glass (boron, alkalis).

These findings all indicate that at high flow rates the leach behavior of the two glasses is similar; however, at moderate flow rates MCC DWRG begins to show a decrease in leach rates as a result of saturation with respect to the major matrix elements and the formation of a protective alteration layer, while a similar effect in the case of SRL TDS-131 glass only takes place at extremely slow flow rates. This is likely to be the result of the larger extent of the pH excursion in the case of SRL TDS-131, which originates in its higher Na content (see Table 1.1). As shown in Table 1.7, at a relatively high flow rate of 11 m/yr the pH values of the leachates of the two glasses are not very different (10.0 and 9.65, respectively), but as the flow rate slows down to 2 m/yr the pH of the DWRG remains virtually unaltered while that of SRL TDS-131 rises to 10.7.

The results of the flow tests presented in this section and in Section 1.5.7 below show that only at flow rates higher than approximately 10 m/yr (where S/V values are of the order of 60 m^{-1}) the steady-state compositions of leachates depend on contact time. At lower flow rates, which encompass the most probable flow rates expected under repository conditions (see Section 1.2.3 and Chapter 3), leaching at various contact times eventually gives rise to nearly the same leachate compositions. This implies, for instance, that if under these conditions the surface area of the glass and the S/V ratio further increase as the result of fracture (Hughes, Marples and Stoneham 1983; Smith and Baxter 1981) the

steady-state leachate concentrations and the ensuing release rates according to eq. (1.9) will not exhibit significant increases.

1.5.4 Solubility Tests

The differences between the two glasses are sharpest under very slow flow or stagnant conditions. Static experiments were carried out at 70°C on large amounts (10 g) of powdered glass in a small volume (about 20 mL) of water. The results at the end of one year are given in Table 1.8 together with the total extent of depletion of each of the glass components based on its initial abundance in the specimen. It can be seen that the large difference in final pH causes SRL TDS-131 to decompose to a very large extent while MCC Reference Glass remains essentially intact under the same conditions. The difference in leachability between the soluble components of the two glasses, respectively, corresponds to a factor of 20 to 100.

TABLE 1.8. Solubility Tests on Defense Waste Glass, 10 g of -60 +200 Mesh Powder in Deionized Water, 70°C, 360 Days

	Final Leachate Concentration, mg/L		Total Dissolved Fraction, %	
	TDS-131	DWRG	TDS-131	DWRG
B	8578	106	93.10	0.76
Na	15662	233	59.55	0.61
Li	1137	137	22.93	1.21
U	n.p.	82.7	n.p.	0.43
Cs	56.4	4.66	3.23	0.16
Si	1754	377	3.16	0.25
Sr	7.48	2.12	0.28	0.06
Ca	2.97	27.5	0.16	0.22
Al	2.07	57.8	0.04	0.25
Mn	3.42	43.8	0.03	0.32
Ti	0.28	2.34	0.02	0.38
Fe	4.74	113	0.02	0.20
pH	12.42	10.67		
Final Volume, mL	30	14		

n.p. = not present in specimen.

1.5.5 Chemically Accelerated Tests

Flow tests were also carried out on MCC DWRG using deionized water as well as low concentrations of NaOH. The results, given in Table 1.9, show that DWRG, like SRL TDS-131, is much more leachable at high pH values, and that the leach rates increase by nearly an order of magnitude when the pH is raised from 9.3 to 12.7. However, when the initial leachant is water, the pH of DWRG leachates is not expected to reach levels above 10 to 10.5 (see 1.5.3 and 1.5.4) unless the flow rates are extremely small, corresponding to contact times exceeding 10^2 years at the expected repository S/V ratios of about 10^2 m^{-1} . Such slow flow rates, which have values lower than 10^{-2} m/yr (Barkatt et al. 1983) are not likely to be relevant to repository conditions, since mass diffusion of water through the repository will probably place a lower limit of approximately 10^{-2} m/yr on the effective rates of water migration according to current work at Catholic University. Under expected service conditions, the ultimate pH level in the case of DWRG is unlikely to exceed the pH of the ground water (around 9.7 in basalt formations, cf., Wood and Salter 1980; Jones 1982) by a considerable extent. On the other hand, in the case of SRL TDS-131 (1.3.3, 1.3.4) the

TABLE 1.9. Dynamic Leach Tests on DWRG, 70°C

	Leachant		
	DI Water	0.05 M NaOH	0.2 M NaOH
pH	9.33	12.7	13.3
Flow rate, m/yr	2.4	2.4	2.4
Normalized leach rate $\times 10^2, \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$			
Si	1.8	14	22
B	2.7	24	37
P	0.76	8.5	12
Li	1.8	25	37
Cs	4.2	24	45
Ca	1.0	0.62	1.4
Sr	0.21	0.088	0.30
Al	1.8	14	25
Mn	0.096	0.014	0.041
Ti	0.084	0.35	1.1
Fe	0.16	0.089	0.27
Ce	<0.05	14	37
U	0.36	1.7	1.4

pH is likely to rise to very high levels (11.5 to 12.5) even when flow rates are not unrealistically slow, overwhelming any buffering by the original ground water composition. Since both glasses are observed to be subject to rapid matrix dissolution when the pH rises above a critical region around 9.5 to 10, as demonstrated in the high-pH buffered tests described in this section, the effective durability of DWRG at slow but finite flow tests is likely to exceed that of TDS-131 by as much as two orders of magnitude since only in the case of TDS-131 is the pH of the surrounding water expected to rise beyond this critical region for the onset of rapid network dissolution (see 1.2.4 and Plodinec, Wicks and Bibler 1982; Wicks et al. 1982). The large difference in leach behavior between the two glasses is caused by a relatively small difference in Na content or Na:Si ratio; however, the slightly higher alkali content of SRL TDS-131 glass is apparently sufficient to prevent buffering of the leached alkali by acidic components of the glass (borate, silicate). The glass composition effects will be discussed in more detail in 1.5.9.

1.5.6 Effects of Temperature, Leachant Composition and Presence of Canister Materials

The effects of leachant composition on the results of dynamic leach tests on DWRG at

70°C were briefly mentioned above (see 1.5.3). The same tests showed that the additional presence of 304L stainless steel with one-third the surface area of the glass had no significant effect on the results.

The results of similar, more extensive experiments carried out at 90°C are given in Tables 1.10 through 1.12 and in Figures 1.26 and 1.27.

The data given in Table 1.10 support the conclusions previously reported in 1.5.3, i.e., that in deionized water the leachate concentrations of the major species first rise quickly with increasing contact time, and then level off at longer contact times. The transition to the saturation region occurs much earlier in the case of DWRG than in the case of TDS-131.

The results obtained in flow tests carried out on DWRG at 70°C in the presence of ground water and/or ductile iron will be discussed in detail in Chapter 3. The purpose of the short discussion of these results in this section is only to point out their relevance to the general mechanistic conclusions based on the studies conducted in deionized water. The target composition of the ground water used in this study was 358 mg/L Na, 3.43 mg/L K, 2.78 mg/L Ca, 0.032 mg/L Mg (most of the magnesium was observed to precipitate out upon standing), 33.4 mg/L F, 312 mg/L Cl,

TABLE 1.10. Results of Dynamic Leach Tests on DWRG in Deionized Water at 90°C

S/Y, m ⁻¹	T _r , Days	Block/ Powder	Leachate Concentration, mg/L										
			pH	Si	B	Na	Li	Cs	Sr	Ca	Al	Fe	U
10.7	4	B	9.04	3.67	0.40	1.25	0.38	0.14	0.031	0.12	0.36	0.05	0.05
30.4	8	B	9.40	11.3	1.48	4.45	1.44	0.35	0.057	0.27	1.26	0.02	0.11
80.9	4	B	9.67	20.7	2.77	8.37	2.24	0.69	0.048	0.22	2.19	0.11	0.29
88.0 ^(a)	4	B	9.84	19.6	3.16	9.57	2.78	0.84	0.035	0.14	1.59	0.17	0.09
157	4	B ^(b)	9.46	18.0	2.45	11.6	2.20	0.79	0.031	0.13	1.72	0.12	0.13
266	4	B	9.87	31.2	4.63	13.8	4.14	1.12	0.039	0.17	3.39	0.29	0.81
291	4	P	9.77	22.8	3.14	9.82	2.82	0.76	0.047	0.20	2.52	0.23	0.73
970	4	P	9.83	28.4	4.12	13.8	3.86	0.87	0.048	0.19	3.09	0.36	0.67
1940	4	P	9.91	30.6	4.63	14.6	4.38	0.93	0.051	0.20	3.33	0.46	0.86
10.7	28	B	9.05	12.1	1.28	3.38	1.26	0.25	0.106	0.46	0.79	0.06	0.21
80.9	28	B	9.70	29.4	3.64	8.68	3.43	0.67	0.065	0.32	2.25	0.15	0.52
88.0 ^(a)	28	B	10.39	28.7	6.94	16.1	6.19	0.77	0.032	0.14	1.96	0.17	0.69
157	28	B ^(b)	9.58	33.1	4.25	11.6	7.75	0.46	0.73	0.35	2.42	0.48	0.83
266	28	B	10.0	50.1	6.90	15.3	6.22	0.78	0.072	0.27	4.05	0.39	0.88
291	28	P	10.01	48.0	6.74	15.2	6.16	0.82	0.084	0.29	3.87	0.37	1.02
970	28	P	10.26	67.2	11.5	24.5	9.73	0.80	0.059	0.21	4.64	0.25	1.23
1940	28	P	10.34	72.0	12.9	29.7	11.9	0.87	0.061	0.25	4.69	0.66	1.45

(a) Iron present; $S_{Fe}/S_{glass} = 1.79$.

(b) Highly polished (3200-grit equivalent; in all other cases 360-600-grit equivalent).

TABLE 1.11. Effects of Ground Water and of Ductile Iron on DWRG Leach Rates in Dynamic Tests, Monolithic Samples, 90°C

S/V, m ⁻¹	T _r , Days	Leachant	$\frac{S_{Fe}}{S_{glass}}$	Leachate Concentration, mg/L									
				pH	Si	B	Li	Cs	Sr	Ca	Al	Fe	U
0.0(a)		GW		9.71	34.7	0.01	0.00	0.00	0.00	4.88	0.05	0.00	0.00
10.7	4	DIW	0.00	9.04	3.67	0.40	0.38	0.136	0.031	0.12	0.36	0.054	0.048
10.5	4	GW	0.00	9.58	35.4	0.14	0.14	0.011	0.044	4.97	0.25	0.001	0.059
10.3	4	GW	2.55	9.89	16.6	0.33	0.29	0.039	0.039	2.22	0.20	6.17	0.041
80.9	4	DIW	0.00	9.67	20.7	2.77	2.24	0.69	0.048	0.22	2.19	0.11	0.29
88.0	4	DIW	1.79	9.84	19.6	3.16	2.78	0.84	0.035	0.14	1.59	0.17	0.09
91.3	4	GW	0.00	9.67	41.6	1.00	0.88	0.25	0.224	4.77	1.38	0.27	0.84
92.0	4	GW	1.71	10.38	28.9	4.27	3.44	1.22	0.308	2.35	1.84	4.21	0.13
266	4	DIW	0.00	9.87	31.2	4.63	4.14	1.12	0.039	0.17	3.39	0.29	0.81
224	4	GW	0.00	9.69	42.4	1.25	1.50	0.38	0.251	4.70	1.51	0.33	1.02
10.7	28	DIW	0.00	9.05	12.1	1.28	1.26	0.25	0.106	0.46	0.79	0.06	0.21
10.5	28	GW	0.00	9.39	36.5	0.32	0.34	0.07	0.093	5.05	0.46	0.00	0.28
10.3	28	GW	2.55	10.64	11.4	1.98	2.00	0.48	0.053	1.03	0.64	1.28	0.04
80.9	28	DIW	0.00	9.70	29.4	3.64	3.43	0.67	0.065	0.32	2.25	0.15	0.52
88.0	28	DIW	1.79	10.39	28.7	6.94	6.19	0.77	0.032	0.14	1.96	0.17	0.69
91.3	28	GW	0.00	9.48	40.0	0.86	0.83	0.21	0.185	3.59	0.74	0.00	0.34
92.0	28	GW	1.71	11.31	51.9	14.05	13.12	2.01	0.299	1.92	3.62	6.02	0.55
266	28	DIW	0.00	10.00	50.1	6.90	6.22	0.78	0.072	0.27	4.05	0.39	0.88
224	28	GW	0.00	9.53	46.7	1.84	1.63	0.33	0.289	4.05	1.17	0.00	0.65

(a) Pure synthetic ground water; Al and B present as impurities; additionally contains 357 mg/L Na, 5.08 mg/L K, 0.014 mg/L Mg, 309 mg/L Cl⁻, 38.6 mg/L F⁻, 190 mg/L SO₄²⁻ and 55 mg/L of (HCO₃⁻ + CO₃²⁻) prepared according to Wood and Salter 1980; Jones 1982.

TABLE 1.12. Effects of Temperature on DWRG Leach Rates in Dynamic Tests, Monolithic Samples

S/V, m ⁻¹	T _r , Days	Leachant	Temp., °C	Leachate Concentration, mg/L									
				pH	Si	B	Li	Cs	Sr	Ca	Al	Fe	U
0.0(a)		GW		9.71	34.7	0.01	0.00	0.00	0.00	4.88	0.05	0.00	0.00
304	4	DIW	70	9.69	19.0	2.52	2.26	0.63	0.024	0.122	2.27	0.03	0.26
266	4	DIW	90	9.87	31.2	4.63	4.14	1.12	0.039	0.173	3.39	0.29	0.81
268	4	GW	70	9.61	36.6	0.41	0.59	0.11	0.078	4.77	0.22	0.11	0.30
224	4	GW	90	9.69	42.4	1.25	1.50	0.38	0.251	4.70	1.51	0.33	1.02
304	28	DIW	70	9.83	34.0	4.47	4.31	0.82	0.091	0.38	3.94	2.22	0.68
266	28	DIW	90	10.00	50.1	6.90	6.22	0.78	0.072	0.27	4.05	0.39	0.88
268	28	GW	70	9.47	36.8	0.45	0.77	0.11	0.110	5.08	0.44	0.07	0.46
224	28	GW	90	9.53	46.7	1.84	1.63	0.33	0.289	4.05	1.17	0.00	0.65

(a) Pure synthetic ground water; cf. footnote a in Table 1.11.

FIGURE 1.26. Results of Dynamic Leach Tests on DWRG, Deionized Water, 90°C, Normalized Concentration Versus $Tr \cdot (S/V)$. Data points in parentheses obtained in the presence of iron, $S_{Fe}:S_{glass}=2$.

FIGURE 1.27. Results of Dynamic Leach Tests on DWRG, Deionized Water, 90°C, Leach Rate (fractional loss rate) Versus Contact Time (equivalent flow rate)

173 mg/L SO_4 , 35.6 mg/L Si, 55.1 mg/L ($HCO_3 + CO_3$), pH 9.77 (Wood and Salter 1980; Jones 1982). Briefly, the data given in Table 1.11 show that the substitution of simulated ground water for deionized water causes a drop by a factor of 3 to 4 in the leach rates of Si and most other glass components. However, species such as Sr and U show enhanced leaching due to the presence of complexing anions (Cl^- , F^- , SO_4^{2-} , CO_3^{2-} , HCO_3^-) in

ground water (cf. Chapters 3 and 4). The presence of ductile iron has little effect on leaching in deionized water, but in silicate ground water it causes a large increase in leach rates of most of the glass components (such as Si, B and the alkalis), except uranium, bringing them to levels which slightly exceed those obtained in deionized water. [Similar results were observed in the case of PNL 76-68 glass (McVay 1982).] The pH of the ground water leachates is also significantly higher in the presence of iron. This is largely due to the effectiveness of iron in removing silica from the aqueous phase. Ductile iron also acts as a very efficient sink for Ca. The increase in leach rates and in pH when iron is present in ground water is much larger at slow flow rates than at high flow rates. The results in ground water support the conclusion that at slow flow rates the concentration of Si in the leachate is controlled by saturation, and that as a result the effective leach rates are lower if the original leachant contains considerable amounts of dissolved silica (see 1.4.3.2 and 1.4.7). When ductile iron is added to the system, it removes silicate from the aqueous phase to form iron silicates on the surface of the solid iron in the form of suspended solid particles. At the same time, the removal of the dissolved silica buffer from the solution causes a significant rise in the pH. Both these factors give rise to significant increases in the effective leach rates of the glass in the saturated and nearly saturated region. The ductile iron used in the flow tests summarized in Table 1.11 contained 3.9% C, 2.43% Si, 0.27% Mn, 0.08% P and 0.005% S. The surface area of the iron was approximately twice the surface area of the glass. The finding that the attack of water on glass slows down when silicate ground water is used as the leachant instead of deionized water but becomes more rapid in the presence of iron is also reflected in differences in the thickness of the gel layer among glass samples leached in the two types of leachant and in the presence as well as in the absence of iron (see Chapters 3 and 4). The atmosphere and the redox conditions under which the experiments on iron-containing systems were carried out are described in Section 1.5.7 below.

Comparison between the data obtained in the flow tests carried out at 70°C and at 90°C, respectively (see Table 1.12) shows that the temperature-dependence parameter is (29 ± 3) kJ in deionized water and (65 ± 7) kJ in ground water at a flow rate corresponding to 12 m/yr. The low value obtained in deionized water, in particular, is closer to the enthalpy of solution than to activation energies of

dissolution of silicate glasses in pure water (1.4.6). The results indicate, in agreement with the other data shown in Section 1.5, that in the case of DWRG leaching saturation is approached at relatively high flow rates and dilutions due to the absence of a very large, persistent pH excursion.

1.5.7 Speciation: Monomeric Versus Aggregated Species, Oxidation States

The measurements on the leach products of DWRG at 90°C using the dynamic test described above included analyses aimed at distinguishing between monomeric and aggregated species (in the cases of Si and Fe) and between oxidized and reduced states (in the cases of Fe and U). The analytical methods consisted of dc plasma spectroscopy, which is used to determine total concentrations, including monomeric and polymeric solutes, colloids and particulate species up to a size of approximately 50 μm , as well as colorimetry, which is sensitive only to dissolved monomeric species (e.g., batho-phenanthroline colorimetry only detects dissolved iron ions). The analytical methods are described by Barkatt et al. (1981). The results of these measurements are given in Table 1.13.

Visible turbidity was persistently observed only in the leach vessels which contained ground water and ductile iron. (In deionized water, turbidity was observed during the

first few days when iron was present, but subsequently the leachates appeared clear.) The color of the turbid leachates was yellow, and they became clear upon acidification.

In considering oxidation states it is necessary to take into account the composition of the gas phase. In cases where deionized water was used as a leachant, boiled water bubbled with nitrogen was used to replenish the sampled volume in tightly sealed vessels by means of a syringe and a septum cap. The vessels were placed in a nitrogen-purged Ascarite®-containing dessicator inside a 90°C oven. As a result, the gas phase is assumed to consist of nitrogen with water vapor and a small fraction of atmospheric air depleted in CO_2 . (Typical dissolved CO_2 levels in the leachate are around 1 mg/L.) In cases where carbonate-rich ground water was used as a leachant, the leachant was introduced at room temperature without passing nitrogen and the tightly sealed leach vessels were placed in an empty dessicator to prevent loss of CO_2 . The gas phase in this case is assumed to consist of atmospheric air highly enriched with respect to water vapor and CO_2 . When ductile iron is introduced into both types of water (particularly ground water) its dissolution is expected to cause the environment to become more reducing. It should be pointed out that the effect of iron on glass dissolution has been shown to be highly dependent on the atmospheric conditions

TABLE 1.13. Speciation of Leached Components of DWRG in Dynamic Tests, 90°C(a)

S/V, m ⁻¹	T _r , Days	Block/ Powder	Leachant	Leachate Concentration, mg/L										
				S _{Fe}		Si		Fe _{total}			Fe ²⁺		U _{total}	
				S _{glass}	pH	DW	CW	DW	CA	CW	CA	CW	CA	U ⁴⁺
10.7	4	B	DIW	0.00	9.04	3.67	3.51	0.03	0.05		0.02		0.05	0.01
80.9	4	B	DIW	0.00	9.67	20.7	22.3	0.05	0.11		0.02		0.29	0.01
88.0	4	B	DIW	1.79	9.84	19.6	24.6	0.17	0.19	0.01	0.05	0.01	0.09	0.01
157	4	B	DIW	0.00	9.46	18.0	17.8	0.12	0.13		0.06		0.13	0.01
266	4	B	DIW	0.00	9.87	31.2	33.2	0.29	0.27		0.14		0.81	0.02
291	4	P	DIW	0.00	9.77	22.8	27.5	0.23	0.26		0.14		0.73	0.02
970	4	P	DIW	0.00	9.83	28.4	32.0	0.36	0.32		0.17		0.67	0.01
1940	4	P	DIW	0.00	9.91	30.6	25.9	0.46	0.30		0.16		0.86	0.01
10.5	4	B	GW	0.00	9.58	35.4	32.7	0.04	0.07		0.04		0.06	0.01
10.3	4	B	GW	2.55	9.89	16.6 ^A	15.3	6.17 ^A	2.29	0.66	0.31	0.08	0.04	0.01
91.3	4	B	GW	0.00	9.67	41.6	39.4	0.27	0.22		0.08		0.84	0.01
92.0	4	B	GW	1.71	10.38	28.9 ^A	27.4	4.21 ^A	3.65	0.67	0.33	0.03	0.13	0.01
224	4	B	GW	0.00	9.69	42.4	40.8	0.30	0.35		0.16		1.02	0.01

(a) D = dc plasma spectroscopy.

C = Colorimetry (absorption spectroscopy).

A = Acidified (to 0.0012 M HNO_3) in the case of DIW, to 0.024 M HCl in the case of GW before analysis. The analysis of U is preceded by acidification to 4 M HCl.

W = Without acidification (samples for dc plasma spectroscopy were not acidified except in the case of groundwater in the presence of iron).

prevailing during the test (Jantzen 1984). It has been demonstrated, for instance, that under completely anoxic conditions both the extent of corrosion of iron and the enhancement of glass dissolution in the presence of iron are much smaller than in oxic environments. The problem of redox conditions in the repository environment and of their effects on the release of glass components is complex. For instance, as shown above, whenever corrosion and oxidation of iron takes place glass leach rates may be enhanced. The effects of ground water composition on the presence of iron and of other waste package materials and of radiolysis on redox conditions and, consequently, on release rates from the glass are discussed in further detail in Chapters 3, 4 and 5.

The results given in Table 1.13 show that within experimental error the results of the colorimetric determinations of Si are identical with the dc plasma data, i.e., that all the silica in the leachate is present in the dissolved monomeric form.

The results of the measurements on iron species in the leachates show that in the cases of deionized water, in the absence as well as in the presence of introduced ductile iron, and in the ground water without iron, about 30% of the iron content of the leachate consists of Fe^{2+} . However, when ductile iron is added to ground water the relative abundance of Fe^{2+} drops to 10% of the total iron content in spite of the more reducing nature of the environment. The absolute concentration of Fe^{2+} is higher when Fe is present, but in the case of Fe^{3+} the increase is more prominent. The results given in Table 1.13 also show that most of the iron in both oxidation states in the leachate is present in the form of aggregates rather than as monomeric dissolved iron species. Only in ground water is it possible to observe appreciable levels of iron in the form of Fe^{3+} , probably because of complexation by anions (Cl^- , F^- ,

SO_4^{2-} , CO_3^{2-}). This explains why the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio is higher in the iron-ground water system.

According to Table 1.13 less than 5% of the uranium in the deionized water and ground water leachates at 90°C is present as U(IV), even in the presence of iron. In a flow test carried out at 70°C in deionized water using DWRG wafers at an S/V ratio of 73 m^{-1} and a residence time of 28 days the concentration of total uranium in the leachate was observed to stabilize at a level of 0.27 ± 0.02 mg/L while the concentration of U(IV) was 0.055 ± 0.005 mg/L, i.e., 20% of the uranium was present as U(IV). The higher temperature of the experiments summarized in Table 1.13 appears to promote the presence of the more oxidized form of the uranium in solution.

1.5.8 Static Tests

The results of a 28-day MCC-1 test carried out on DWRG at 90°C ($\text{S/V} = 10 \text{ m}^{-1}$) are compared with those of a flow test conducted under similar conditions (90°C, $T_r = 28$ d, $\text{S/V} = 10 \text{ m}^{-1}$) in Table 1.14. It can be seen that the results of the static test at short periods diverge from those of the dynamic test because of the strong effects of transients which are retained in the leachate composition obtained in the static test. Moreover, a static test conducted over a single period of exposure provides less kinetic information than a dynamic test which includes numerous periodic samplings. However, at long times the results of the static test approach those of the dynamic test due to the diminishing importance of the results of the initial transients on the static test leachates (see Section 1.3.8).

1.5.9 Effects of Glass Composition - Comparison of TDS-131 Glass with DWRG

Based on the experimental findings cited in this section, it can be concluded that the

TABLE 1.14. Comparison of the Results of MCC-1^(a) and Dynamic^(b) Leach Tests on DWRG, 90°C, Monolithic Samples

Type of Test	S/V, m^{-1}	T, Days	Leachant	pH	Leachate Conc., mg/L				
					Si	B	Sr	Fe	Na
A	10.0	28	DI water		23.5	2.54	0.104	0.176	8.82
B	10.7	28	DI water	9.04	12.5	1.40	0.096	0.058	4.18

(a) Pacific Northwest Laboratory.

(b) The Catholic University of America.

leach behavior and the controlling leach mechanisms of borosilicate glasses at a given temperature are not only strongly dependent on leachant composition and on flow/dilution conditions, but also sensitive to relatively small changes in glass composition.

A relatively small increase in alkali content can cause, according to the findings listed above, an enhancement of the pH excursion upon leaching and it can inhibit the onset of saturation at moderately slow flow rates. In such cases leaching is not retarded until contact between the leachant and the glass has lasted for long periods or until the glass undergoes decomposition to a large extent. Thus SRL TDS-131, although close in composition to DWRG and exhibiting leach rates which are only slightly higher at high dilutions, undergoes more extraction of its soluble components upon prolonged contact with a given volume of water than DWRG, which is much more durable at long contact times.

Quantitatively, the large differences in leach behavior between TDS-131 and DWRG can be interpreted on the basis of the molar composition of the original glass and of the leachate obtained at the longest residence time in the two cases (see Table 1.15). The mole fraction X^g of each of the principal components of the glass is divided by X_B^g , the

mole fraction of boron which is always the most leachable element (Wallace and Wicks 1983). The difference between the molar amounts of each species relative to boron in the leachate (X^l/X_B^l) and in the solid glass (X^g/X_B^g), respectively, serves as an indicator of the amount of that species which stays behind in or on the leached surface (X^s) during the leaching process, i.e., $X^s/X_B^g = X^g/X_B^g - X^l/X_B^l$ (Barkatt et al. 1984b). The results of this calculation in the cases of TDS-131 and of DWRG are given in Table 1.15. It can be seen that in the case of DWRG the total relative amount of alkalis in the leachate ($X^l/X_B^l = 2.5$) is smaller than that of the buffering species silicate ($pK = 9.7$) and borate ($pK = 9.1$), for which the combined value of X^l/X_B^l is 3.7. On the other hand, in the case of TDS-131 the relative amount of alkalis in the leachate, 1.7, exceeds the corresponding combined amount of silicate and borate, 1.6, and this leads to a pH rise under slow flow or stagnant conditions, and to an accelerated decomposition of the glass. Under the same conditions DWRG exhibits a stabilized pH level around 10 and a much smaller degree of attack on the glass.

As regards the composition of the two glasses themselves, according to Table 1.15 SRL TDS-131 contains only a combined mole fraction of 0.49 of the two acidic oxides SiO_2

TABLE 1.15. Molar Compositions of the Glass and of the Saturated Leachant (Relative to Boron) and Resulting Surface Compositions for TDS-131 and DWRG

Component	SRL TDS-131				DWRG			
	Original Glass		Saturated Leachate	Surface Remainder	Original Glass		Saturated Leachate	Surface Remainder
	X^g	X^g/X_B^g	X^l/X_B^l	X^s/X_B^g	X^g	X^g/X_B^g	X^l/X_B^l	X^s/X_B^g
SiO_2	0.356	2.55	0.5	2.05	0.458	4.1	2.3	1.8
$1/2 B_2O_3$	0.137	1.0	1.0	0.0	0.111	1.0	1.0	0.0
$1/2 Na_2O$	0.195	1.35	1.05	0.3	0.137	1.2	1.1	0.1
$1/2 Li_2O$	0.122	0.9	0.6	0.3	0.142	1.3	1.2	0.1
$1/2 Fe_2O_3$	0.088	0.6	0.0	0.6	0.068	0.6	0.05	0.55
$1/2 Al_2O_3$	0.036	0.25	0.0	0.25	0.058	0.5	0.2	0.3
MgO	0.017	0.1	0.0	0.01	0.005	0.1	0.0	0.01
MnO ₂	0.024	0.2	0.0	0.2	0.021	0.2	0.0	0.2
NiO	0.019	0.15	0.0	0.15	0.014	0.15	0.0	0.15
CaO	0.007	0.05	0.0	0.05	0.017	0.15	0.0	0.15
SrO	0.004	0.05	0.0	0.05	0.002	0.02	0.0	0.02
TiO ₂	0.005	0.05	0.0	0.05	0.001			
ZrO ₂	0.001				0.004	0.05	0.0	0.05
$1/3 U_3O_8$					0.005	0.05	0.0	0.05

and B_2O_3 . More than one-half of the glass composition is made of basic oxides which are either highly soluble (Na_2O , Li_2O) or tend at low flow rates to form insoluble silicates and thereby reduce the levels of dissolved silica which can buffer the solution against a pH runaway effect. On the other hand, DWRG contains a significant excess of acidic oxides (a mole fraction of 0.57) over the combined basic oxides in the glass, and this is sufficient to moderate the pH rise as the glass dissolves even at low flow rates.

The calculations shown in Table 1.15 also assist in predicting the compositions of alteration products formed in or on the surface. Neglecting minor species, the surface composition obtained in the case of TDS-131 glass corresponds to $Ca(Na,Li,Cs)(Fe,Al)Si_2O_6$. The two most frequently cited alteration phases, acmite (aegirine) and analcime (see 1.4.3, 1.4.5), fall within this composition range. In the case of DWRG the ratio between (Fe,Al) and Si is very similar to the ratio obtained in the case of TDS-131 but the concentration of alkali metal ions is much lower, indicating a more clay-like character of the surface solid. It should be emphasized that the altered surface compositions calculated in Table 1.15 refer only to long contact times, i.e., to slow flow rates. As detailed above in the case of both glasses, at high flow rates not only boron and the alkalis but also Si and Al dissolve congruently, and only very insoluble species such as Fe, Mn and Ni stay behind due to the lower degree of saturation and the lower pH of the corresponding leachates. Under high-flow conditions iron oxides such as hematite, for instance, rather than iron silicates or aluminosilicates, can be calculated to be the likely alteration products (see next paragraph). The mass balance calculations represented by Table 1.15 should be considered in conjunction with the results of direct analysis of the leached surfaces (Chapter 2).

Under rapid-exchange conditions (Table 1.6) the leach rates of all the major components of DWRG are similar to, or slightly lower than, the corresponding leach rates in the case of TDS-131. As emphasized above, at moderate flow rates (Table 1.7) and, in particular, under stagnant conditions (Table 1.8) the leach rates of Si, B and the alkalis from DWRG are much smaller than those of TDS-131 due to the absence of a very large pH rise and the consequent slower attack on the glass matrix. However, under the latter conditions the leach rates of divalent and polyvalent metals with a large charge density (charge-to-size ratio, see Barkatt, Simmons and Macedo 1981), such as Ca, Al, Mn, Ti and

Fe, are much higher in the case of DWRG. This may be due in part to precipitation of hydroxides or oxides (Ca solubility, in particular, is extremely dependent upon pH) at the higher pH encountered in near-saturated TDS-131 leachates, and in part to formation of less soluble compounds with silicate. In the case of Al, for instance, it is well-known (Barkatt et al. 1982) that the concentrations in solution steadily decrease upon increase in the levels of silicate, which is present at much higher concentrations in TDS-131 leachates. Strontium, which has a relatively low charge density, is an intermediate case between Ca and the heavier alkalis such as Cs. Cesium itself displays retarded leaching at long contact times which may be attributed to selective resorption and reprecipitation promoted by the lower solubility of silicates and aluminosilicates of the heavier alkali ions in high-pH media (Barkatt et al. 1982; 1984b). Although the concentrations of Al, Fe, etc., in solution are too small to control the concentration of dissolved Si, they are likely to be important in determining the nature of the alteration products of the leached surface (cf. Table 1.15). It should also be noted that DWRG, unlike the TDS-131 glass samples used in the present study, contains a significant fraction (2.8%) of U_3O_8 (see Table 1.1). However, it is difficult to attribute the differences in leach behavior between the two glasses primarily to the presence of U in one of them. As shown in Section 1.5.6, the enhanced leaching of uranium in ground water is accompanied by retardation of the dissolution of most of the major glass components. Furthermore, uranium oxides are not expected to cause a large reduction in the extent of the pH excursion, which is (as noted above), a major factor in determining the leachability under slow-flow and stagnant conditions. As shown below (Section 1.6) the relative leachability of both TDS-131 and DWRG under slow-flow conditions agrees well with observations on other uranium-containing and uranium-free glasses when it is assumed that slow-flow leach behavior is primarily determined by the relative abundances of basic oxides and acidic oxides in the glass composition.

The most important conclusion of this section is that relatively minor changes in glass composition can cause large differences in the pathway and rates of corrosion. A similar conclusion has been reported in studies of TDS-131 glass doped with very small amounts of simulated fission products and actinides (Bates, Lam and Steindler 1983). The large effects of glass composition are due to the fact that several mechanisms are involved in the corrosion process (Barkatt et

al. 1982). A small increase in the amount of alkalis and a corresponding small decrease in silica content can lead to a large pH excursion. This results in a large increase in the extent of the range of conditions where matrix dissolution is the controlling mechanism and to a suppression of the onset of saturation, which limits the concentration of leached species and slows down the net loss of material from the glass.

1.5.10 High-Temperature Studies: Equilibrium Reactions and End Product Phases

1.5.10.1 Time-Temperature-Transformation Relationships

Most studies of the interaction of the MCC Defense Waste Reference Glass (and other glasses proposed for disposal of radioactive waste) with leachants have been conducted at temperatures lower than the boiling point of water. A study carried out by White and co-workers at the Pennsylvania State University was initiated to see if the results at the lower temperatures can be smoothly extrapolated into the higher temperature regime. At high temperatures, crystalline reaction products are clearly present (and abundant). One question concerning crystallization processes is of great interest in the study of glass-water interactions in the 40 to 90°C temperature range which is most relevant to the present study. This question is whether the same crystalline reaction products can be expected at the lower temperatures and if so, after what duration.

In order to understand (at least empirically) the reaction(s) and to extrapolate the results, it is necessary to have a quantitative description of the results; toward this end, we have chosen to adapt an approach used by metallurgists, a T-T-T plot (time-temperature-transformation). For this plot, some observed property of the reaction (transformation) is plotted and contoured against a function of time [$\log(t)$] and of temperature ($1/T$); this choice of functions comes from the model provided by the Arrhenius relation for a zeroeth order reaction. For this ideal case, the relation between time, temperature and transformation (concentration in solution) is:

$$\ln[C(t) - C(t_0)] = \ln(t) - E_a/RT + A \quad (1.14)$$

where t is time, T is temperature, C is concentration, E_a is activation energy, and A is a constant. For this model, contours of concentration would be straight lines, spaced logarithmically. A second reaction mechanism comes to dominate the reaction at longer

times, the crystallization of reaction products. For the simple model of crystal growth starting and continuing with minimal supersaturation, the contours of concentration on the T-T-T plot would exhibit a break in slope at the initiation of crystallization (approximately when saturation is reached). After crystallization has started, the concentration contours should be more nearly constant, they will become constant when the phases being precipitated equal the material being removed from the glass. If the solubility products of the crystalline phases were constants independent of temperature, then the sums of the logarithms of the concentrations of the participating species, weighted according to the stoichiometry, would be a constant, not the individual concentrations.

After the solution concentrations have reached saturation with respect to one or more crystalline phases, the abundance of that phase(s) should increase steadily and could be contoured. The spacing of the contours would be related to the rate of supply of the limiting element which may change as additional phases start to precipitate.

The experiments were performed by sealing (welding) polished slabs of glass and water in gold tubes and then running the experiments in conventional cold seal pressure vessels. The vessels were quenched by removing the pressure vessel from the furnace and allowing it to cool spontaneously. The capsule was then removed and opened, the glass slab was removed and the solution collected for analysis. The solution was diluted, centrifuged if there was any indication of particulate material, and then acidified for storage until analysis. The major elements were analyzed by atomic emission spectroscopy with a dc plasma source, except for cesium (atomic absorption spectroscopy with a flame source) and uranium (laser-excited fluorimetry). The glass slice was rinsed with ethanol and dried with a blast of freon. The initial examination of the glass slice (and the interior of the capsule) was with a binocular dissecting microscope (to 80X). For samples with thick alteration rinds or crystals growing on the surface, further examination was by SEM/EDX on the outer surface and on a fractured surface. The samples with thinner alteration zones have not been examined yet, and a combination of SIMS or infrared spectroscopy is proposed for their examination.

Complete details of the experimental procedure are given by Freeborn and White (1984). The results of the solution analysis are detailed in Section 1.5.10.2, and the crystalline phases identified are described in Chapter 2 and listed in Table 2.6.

Returning to the question of the correlation between the results of the high-temperature crystallization experiments (100 to 250°C) detailed above and the alteration behavior at the lower temperature range of interest (70 to 90°C), it can be concluded that the transition between the two temperature ranges appears to be smooth with respect to the nature of the alteration products and the time required for their appearance. Most of the alteration products observed at the high temperature range, e.g., analcime, weeksite and silicates of Ca and of transition metal ion silicates (see Table 2.6) also appear in the lower temperature range (see Table 2.5). Tobermorite or similar calcium silicates, listed in Table 2.5, were identified in high-temperature alteration studies on both TDS-131 glass (see 1.4.5 and Bates and Steindler 1983) and DWRG (see Table 2.6). High-silica alteration phases have also been observed at both temperature ranges.

As regards the length of the period required for the formation of the alteration products, it was already mentioned in Section 1.4.5 that extrapolation of the T-T-T plot to lower temperatures in the case of TDS-131 indicates that the appearance of visible crystals takes somewhat longer than the stabilization of the composition of the leachate in steady state with respect to the altered surface. This is to be expected when it is assumed that control of the composition of the solution by the altered surface phase does not require the development of a macroscopic crystallized phase. In the case of DWRG the results of observations on the time required for the appearance of visible crystals are summarized in Figure 1.28. As in the case of TDS-131, extrapolation of the data on DWRG to lower temperatures yields a time of approximately 4 years at 90°C and of approximately 20 years at 70°C. [A more accurate comparison is not possible because of large experimental uncertainties, especially in the case of TDS-131 (see Section 1.4.5).] In general, it appears at present that the results of high-temperature studies on the two glasses are not very different, and that their extrapolation to lower temperatures is compatible with the results of surface characterization studies and of kinetic studies conducted at temperatures below 100°C.

1.5.10.2. Solution Compositions in High-Temperature Experiments

Two series of experiments were performed in which DWRG was reacted with deionized water at temperatures and pressures above the normal boiling point of water. As detailed in Section 1.5.10.1, there were two objectives

FIGURE 1.28. T-T-T Plot of the Formation of Crystalline Products (DWRG)

to these studies, viz. to investigate the solution composition (leaching) as a function of time and temperature, and to establish the conditions necessary to produce crystalline phases (saturated solutions) and to study the effect of this crystallization on the leach behavior.

The experimental techniques employed in this study followed the usual practices employed with closed capsules and cold seal pressure vessels (Freeborn and White 1984). The usual limitations of small sample volumes and the possibility of reactions occurring during the quenching process apply to these studies, but the results demonstrate that there are significant effects associated with the higher temperatures which can be observed in spite of any complications caused by the experimental technique.

The run conditions for each of the experiments are listed in Table 1.16 and the results are shown in Figure 1.28 for the experiments with 0.1 g of water. The results of the solution analyses are shown in Tables 1.17 and 1.18. The crystalline reaction products are discussed in Chapter 2; the line across Figure 1.28 is the boundary separating the conditions where no crystalline reaction products were recognized (below the line) and where they were found (above the line).

Five elements were consistently detected at levels above the detection limit (B, Li, Na, Si and U) and two more were generally present above the detection limit (Al and Ca, although these two elements were never observed to be present at levels in a large excess over the detection level). The cations of the remaining oxides in the glass formulation were generally present at levels below the detection limits in solution.

TABLE 1.16. Experimental Run Conditions for the Reaction of DWRG with Deionized Water Under Hydrothermal Conditions

Run No.	Temp., °C	Time, hr	Run No.	Temp., °C	Time, hr	H ₂ O, g
3 A	95	302.2	24 C	25	1900.0	1.003
3 B	148	250.2	24 F	25	1900.0	0.297
3 C	201	157.5	22 F	119	105.0	0.099
3 D	247	102.2	23 A	119	105.0	0.301
4 A	199	49.8	21 C	118	360.0	0.105
4 B	164	307.6	25 A	118	360.0	0.297
4 C	250	24.5	20 A	118	360.0	0.997
5 A	170	477.1	23 E	138	1800.0	0.104
5 B	129	476.6	20 D	138	1800.0	0.300
5 D	94	527.1	24 B	138	1800.0	0.990
6 A	148	31.0	21 A	178	72.0	0.097
6 B	129	164.0	23 C	178	72.0	0.295
6 C	112	164.1	22 D	178	72.0	1.004
6 D	148	947.9	21 B	175	360.0	0.099
7 A	93	370.7	23 D	175	360.0	0.301
7 B	121	369.8	20 B	175	360.0	1.005
7 C	100	371.4	24 E	174	1800.0	0.100
8 A	99	192.5	24 D	174	1800.0	0.296
8 C	150	85.8	24 A	174	1800.0	1.000
8 D	126	949.7	21 E	220	71.0	0.095
9 A	200	27.1	23 F	220	71.0	0.297
9 B	105	85.7	23 B	225	361.0	0.290
9 C	152	84.8	22 C	225	361.0	1.001
9 D	166	949.5	20 F	230	1800.0	0.098
			20 E	230	1800.0	0.302
			20 C	230	1800.0	1.002

TABLE 1.17. Solution Analyses for the Reaction of DWRG with Water. Concentrations in mg/kg H₂O; 0.10 g H₂O and one face polished.

Run No.	Time, hr	Temp., °C	Al	B	Ca	Cs	Fe	Li	Mg	Mn	Na	Ni	Si	Sr	Zr	U
7 A	370.75	93	<5.2	7.8	15.6	<13.0	<5.2	20.7	7.8	<5.2	38.9	<5.2	77.8	<5.2	<13.0	4.850
3 A	302.25	95	10.6	10.6	7.9	<13.2	23.8	13.2	<5.3	<5.3	39.7	<5.3	63.6	<5.3	<13.2	2.834
7 C	371.42	100	12.9	15.4	12.9	<12.9	5.1	38.6	<5.1	<5.1	69.5	<5.1	144.2	<5.1	<12.9	9.011
9 B	85.70	105	36.7	<5.2	162.5	97.0	7.9	13.1	47.2	<5.2	52.4	<5.2	448.1	<5.2	<13.1	3.983
6 C	164.08	112	<4.9	14.8	19.8	<12.4	<4.9	29.6	4.9	<9.9	61.8	<4.9	118.6	<4.9	<12.4	0.642
7 B	369.83	121	<5.0	<5.0	17.3	<12.4	<5.0	22.3	<5.0	<5.0	34.7	<5.0	59.5	<5.0	<12.4	3.816
8 D	949.72	126	29.7	14.9	57.0	<12.4	<5.0	32.2	9.9	<5.0	79.3	<5.0	123.9	89.2	<12.4	3.915
6 B	163.97	129	18.4	18.4	21.1	<14.5	<5.3	42.1	<5.3	<5.3	73.8	<5.3	176.5	<5.3	<13.2	3.872
6 A	31.08	148	16.9	26.5	<4.8	<12.1	<4.8	36.2	<4.8	<4.8	89.2	<4.8	156.7	<4.8	<12.1	3.230
3 B	250.25	148	15.2	43.0	35.4	<12.7	22.8	48.1	15.2	<5.1	141.7	<5.1	235.3	<5.1	<12.7	11.640
6 D	947.92	148	23.4	38.9	41.5	<13.0	<5.2	44.1	<5.2	<5.2	127.2	<5.2	220.7	85.7	<13.0	4.699
8 C	85.78	150	52.2	32.3	19.9	<12.4	27.3	49.7	7.5	7.5	111.8	5.0	546.7	<5.0	<12.4	8.946
9 C	84.85	152	43.9	29.3	31.7	56.1	19.5	48.8	9.8	4.9	114.6	<4.9	551.2	<4.9	<12.2	19.512
9 D	949.55	166	40.6	334.7	60.9	<12.7	5.1	218.1	12.7	<5.1	649.1	<5.1	925.5	81.1	<12.7	3.245
9 A	27.08	200	33.2	114.8	10.2	<12.8	15.3	107.1	<5.1	<5.1	326.5	<5.1	548.5	<5.1	<12.8	6.888
4 A	49.75	199	17.6	195.6	22.6	<12.5	12.5	125.4	<5.0	<5.0	401.2	<5.0	564.2	<5.0	<12.5	8.275
3 C	157.50	201	15.1	3474.3	5.0	<12.6	<5.0	1284.0	<5.0	<5.0	4405.8	<5.0	1409.9	<5.0	<12.6	14.602
3 D	102.17	247	17.7	7315.8	22.7	15.1	15.1	113.5	<5.0	<5.0	8324.9	<5.0	1337.0	12.6	<12.6	39.102

TABLE 1.18. Solution Analyses for the Reactions of DWRG with Water. Concentrations in mg/kg H₂O; 0.01 g H₂O and both faces polished.

Run	No.	Time, hr	Temp., °C	Al	B	Ca	Cs	Fe	Li	Mg	Mn	Na	Ni	Si	Sr	Zr	U
24	C	1900	25	<0.5	2.5	1.2	<1.2	<0.5	<1.2	<0.5	<0.5	5.2	<0.5	2.7	<0.5	<1.2	0.030
24	F	1900	25	<1.7	13.5	<1.7	<4.2	<1.7	<4.2	<1.7	<1.7	13.5	<1.7	7.6	<1.7	<4.2	0.042
22	F	105	119	7.6	20.2	20.2	<12.6	<5.1	20.2	<5.1	<5.1	45.5	<5.1	96.0	<7.6	<12.6	0.884
23	A	105	119	6.6	16.6	5.0	<4.2	<1.7	12.5	1.7	<1.7	41.5	<1.7	90.5	<2.5	<4.2	1.179
21	C	360	118	7.1	59.5	9.5	19.0	<4.8	14.3	<4.8	<4.8	59.5	<4.8	133.3	<4.8	<11.9	2.738
25	A	360	118	9.3	27.8	3.4	<4.2	2.5	16.8	<16.8	<1.7	53.0	2.5	105.2	<1.7	<4.2	2.104
20	A	360	118	7.3	13.5	2.5	1.5	6.3	14.8	0.8	1.3	37.6	0.8	95.8	0.5	<1.3	2.508
23	E	1800	138	12.0	72.1	7.2	<12.0	19.2	55.3	<4.8	<4.8	125.0	<4.8	240.4	<7.2	<12.0	8.654
20	D	1800	138	7.5	100.0	6.7	<4.2	12.5	85.0	<1.7	3.3	212.5	<1.7	391.7	<1.7	<4.2	3.667
24	B	1800	138	<0.5	53.5	1.5	<1.3	4.5	50.0	0.5	2.0	131.3	<0.5	287.9	<0.5	<1.3	5.808
21	A	72	178	20.8	98.7	33.8	<13.0	18.2	62.4	7.8	<5.2	223.4	5.2	309.2	5.2	<13.0	17.666
23	C	72	178	14.4	72.0	6.8	<4.2	3.4	66.1	1.7	<1.7	213.6	<1.7	328.8	<2.5	<4.2	13.136
22	D	72	178	16.2	35.6	2.0	1.2	3.0	32.4	0.5	<0.5	99.6	5.7	249.0	<0.7	<1.2	9.462
21	B	360	175	5.1	1237.4	37.9	<12.6	7.6	449.5	<5.1	<5.1	2070.7	<5.1	883.8	7.6	<12.6	3.384
23	D	360	175	2.5	129.6	5.0	4.2	1.7	98.8	<1.7	<1.7	290.7	<1.7	481.7	<2.5	<4.2	2.076
20	B	360	175	11.9	63.4	0.7	1.7	<0.5	61.0	<0.5	<0.5	194.0	<0.5	373.2	0.5	6.5	3.856
24	E	1800	174	7.5	5525.0	102.5	<12.5	<5.0	1825.0	50.0	<5.0	7250.0	<5.0	1275.0	10.0	<12.5	20.000
24	D	1800	174	4.2	1444.3	12.7	<4.2	<1.7	574.3	<1.7	<1.7	2060.8	<1.7	954.4	<1.7	<4.2	14.358
24	A	1800	174	1.7	290.0	0.5	2.0	<0.5	147.5	<0.5	<0.5	507.5	<0.5	582.5	<0.5	<1.3	2.500
21	E	71	220	23.7	1868.4	<5.3	<13.2	10.5	676.3	<5.3	<5.3	2736.8	<5.3	1078.9	<7.9	<13.2	0.737
23	F	71	220	<1.7	161.6	5.1	<4.2	6.7	101.0	<1.7	<1.7	333.3	<1.7	538.7	<2.5	<4.2	4.377
23	B	361	225	4.3	2758.6	26.7	<4.3	2.6	801.7	<1.7	<1.7	3793.1	<1.7	1069.0	<2.6	<4.3	40.617
22	C	361	225	1.0	649.4	2.0	1.2	1.5	277.2	<0.5	<0.5	1073.9	<0.5	849.2	<0.7	<1.2	4.995
20	F	1800	230	20.4	24234.7	63.8	33.2	96.9	2678.6	7.7	20.4	25510.2	23.0	2117.3	23.0	12.8	30.612
20	E	1800	230	5.9	9710.3	21.1	11.0	4.2	1266.6	<1.7	<1.7	13932.1	1.7	1165.2	16.0	5.9	9.710
20	C	1800	230	1.5	2619.8	6.5	15.7	1.0	541.4	<0.5	<0.5	4116.8	<0.5	998.0	2.7	3.0	6.234

Aluminum, calcium and uranium were similar in their behavior in that they all were present at low levels in the solution. Their concentrations increased only slightly with temperature and appeared to reach their maximum quite early. There was a general pattern of decrease in concentrations in the experiments which employed a greater proportion of water. This trend exceeded the "correction" obtained by scaling time with the ratio of surface area to solution volume (S/V).

Boron, lithium, sodium and silicon showed a sharp rise of the concentrations in the solution with both increasing temperature and increasing time. The lower concentrations in the experiments carried out with larger quantities of water were compensated for when the product of time and S/V ratio was used instead of time alone. The only deviation from this general pattern was the case of silicon in the series of experiments around 225°C, where silica appeared to have reached the saturation level after 15 days in experiments with 0.1 g H₂O. Despite the similarities in the patterns of concentration as a function of time for these four elements, there were significant differences when they were compared with one another. At low temperatures (less than about 150°C) or at short times at higher temperatures, silicon was found to be more abundant than boron in solution on an atom basis although less than it is in the

glass; at higher temperatures and longer times, boron became more abundant in solution than silicon on an atom as well as weight basis. The same pattern applied to the relationship between lithium or sodium and silicon, silicon being more abundant (although not in proportion to its abundance in the glass) in solution at low temperatures or for short times at higher temperatures. Lithium and sodium accumulated in solution at about the same rate (on an atom basis) as boron except in the case of highest temperatures and longest times, where boron was much more abundant than the other two; the equivalent levels of boron, lithium and sodium in solution in the latter case mean that boron was dissolved in preference to the two alkalis, which were present in the original glass at higher molar fractions than boron (cf. Section 1.5.4 and 1.5.9). Lithium showed a stronger contrast with boron than sodium at the highest temperatures. In general, sodium and lithium concentrations were approximately the same except in the experiments carried out at the highest temperature and the longest time, where sodium was more abundant than lithium. (Similar behavior was observed in the case of long-term solubility studies on TDS-131, cf. Table 1.8.)

The different behavior of the various elements in solution can be partially, but not

entirely, explained by the growth of crystalline phases. Calcium, aluminum and uranium behaved as if they were controlled by saturation under almost the entire range of conditions investigated, although crystalline phases were observed in only about one-half of the experiments.

Once crystals were recognized (at low number densities in runs close to the boundary between the two regions in Figure 1.28), they rapidly increased in number and size. This suggests that failure to recognize the first crystals is not the likely explanation for the saturation behavior in the absence of a saturating phase. The other possibility is that the altered layer is behaving as a saturating phase (see Section 1.6.10.1). This is not inconsistent with some of the observations in Chapter 2, which indicate that in the case of DWRG the development of the crystalline phases does not significantly affect the saturation levels.

Sodium and silicon continued to increase in concentration even after significant quantities of phases such as analcime, wecksite and the various calcium silicates had crystallized. The explanation for this behavior appears to be that it is the supply of aluminum, uranium and calcium, respectively, which controls the growth rate of the several crystalline phases. At the highest temperatures and longest durations the additional phases which are called "silica" in Table 2.6 appeared. These phases appeared to affect the concentrations of lithium and silicon (and to a lesser extent sodium). Boron was found in the analcime phase, but not in sufficient amounts to affect the build-up of boron in the solution.

The differences in the rates of release of the various elements into the solution in the early stages must accordingly be explained in terms of the mechanisms of the reaction of the glass with the water and effective solubility or sorption capacity of the altered glass layer for the different elements.

In general, the conclusions from the solution analysis of the high-temperature leachates agree with the results of leaching studies at lower temperatures described elsewhere in this chapter. Both sets of experiments appear to show that at long contact times the composition of the leachates appears to reflect an initial alteration of the surface, rather than full development of distinct crystalline phases. (However, steady-state concentrations in the aqueous phase may theoretically decrease further in the long run as more stable alteration phases are formed, see

Apted 1982.) Furthermore, experiments above and below 100°C show the same patterns of concentration build-up of the various glass components in the solution. U, Ca and Al are present in relatively low concentrations even at leachates obtained at short contact times, and the relative rates of accumulation of Si, Li and, finally, Na in the solution successively fall behind the rate of boron build-up as contact times are increased.

1.6 OTHER WASTE GLASSES AND NATURAL ANALOGS

SYNOPSIS

In the previous section the comparative leach characteristics of two defense waste borosilicate glasses were documented in detail. It was concluded that moderate increases in silica content and corresponding decreases in alkali oxide content improve the durability of such glasses only slightly in the rapid flow range, but the corresponding reduction in corrosion rates under slow flow or stagnant conditions is extremely large due to suppression of the pH excursion. The present section provides additional evidence for these conclusions and shows that they are generally valid over a broad range of glass compositions. Studies of the leach behavior of natural materials such as tektites, basalt and granite, as well as studies of ancient glasses, furnish important confirmation and validation of conclusions based on short-term tests of defense glasses. They indicate that matrix dissolution at high flow rates and pH-dependent saturation with respect to silica and alumina and reprecipitation at low flow rates are the major mechanisms controlling glass dissolution in the long term as well as in the short term. Studies of natural and ancient glasses also show an excellent agreement with the trends observed in measurements of leach rates of modern glasses with respect to the dependence of durability of glass composition.

1.6.1 PNL 76-68

The composition of PNL 76-68 glass, a leading model glass for commercial waste immobilization (Mendel et al. 1977; Ross et al. 1978) is given in Table 1.1. This glass contains slightly less silica than TDS-131, similar amounts of Na₂O and B₂O₃, and no Li₂O. The mole ratio of Na+Li to Si+B, which appears to influence to a large extent the ultimate alkalinity of the leachate, has a value of 0.44 in the case of PNL 76-68 as compared with 0.49 in the case of DWRG and 0.63 in the case of SRL TDS-131. In agreement with these values, the leachates of PNL 76-68 in deionized water under saturation conditions reach pH

values of approximately 10.5 (Fullam 1982) in similarity to DWRG leachates. These values are much lower than the maximum pH levels of 12.5 obtained in the case of TDS-131. Other distinctive features of PNL 76-68 glass composition are the absence of Al and Mn and the presence of significant amounts of rare earths, Zn and Ti.

Upon exposure to water, PNL 76-68 glass exhibits at high flow rates leach rates which are higher by a factor of 2 than those of TDS-131 at the shortest contact times included in Table 1.19 ($T_r \cdot (S/V) = 48 \text{ d} \cdot \text{m}^{-1}$). However, at long contact times the leach rates of PNL 76-68 become lower than those of SRL-131 (by a factor of approximately 3 when $T_r \cdot (S/V)$ is $22900 \text{ d} \cdot \text{m}^{-1}$), reflecting the more moderate rise in pH in the case of PNL 76-68. It should be noted that the differences in long-term durability between the two glasses do not appear in short term static tests, in which the behavior of the two glasses is almost identical. The dissolution rates of PNL 76-68 based on Si at the end of 7 and 28-day exposures are 1.47 and $0.94 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, respectively (Freeborn and White 1984) while the corresponding rates in the case of TDS-131 are 1.52 and $0.96 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, respectively (Plodinec, Wicks and Bibler 1982). The consequences of the pH rise in the case of TDS-131 are revealed only in tests with long contact times which provide for suppression of initial transient effects.

At short contact times, PNL 76-68 glass appears to acquire a thicker and more stable hydration layer than either TDS-131 or DWRG (Barkatt et al. 1984b; Strachan 1982)^(a). This, however, does not seem to have a major impact on its leach behavior at slow flow rates, compared with that of the defense waste glasses. Moreover, the relative leach rates of the various glass components follow

(a) Also Barkatt et al. "Leach Mechanisms of Borosilicate Glass Waste Forms--Effects of Composition." To be published.

the same kinetic patterns in both cases, e.g., Cs and, in particular, Sr exhibit retarded leaching at slow flow rates due to the factors discussed in 1.5.9.

1.6.2 PGM and CUBS

The composition of PGM, a high-silica borosilicate defense waste glass is given in Table 1.1. This glass does not contain Li, and the $[\text{Na}+\text{Li}]/[\text{Si}+\text{B}]$ ratio is 0.084, a ratio which is lower by a factor of 5 to 7.5 than corresponding values in the cases of PNL 76-68, SRL TDS-131 and MCC DWRG (see 1.6.1). The leach rates obtained in a 1-year frequent-exchange modified-IAEA test at 90°C for Si, B, Cs and Sr are 0.050, 0.063, 0.02 and $0.033 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, respectively (Houser and Pantano 1984), i.e., rates which are lower by one order of magnitude than those obtained for TDS-131. Similarly, low leach rates for PGM were obtained in 28-day MCC-1 static tests (0.007, 0.013, 0.03 and $0.031 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) (Stone 1982; Houser and Pantano 1984) and in dynamic tests at both short and long contact times (Table 1.20). In particular, an MCC-3 solubility test on PGM at 90°C showed that the pH of the leachate did not rise beyond 7.8, and that the levels of dissolved Si, Cs, Sr, Na, Al, and U were 45.2, 0.096, 0.033, 13.8, 5.32 and 0.033 mg/L , respectively. It can be concluded that the long-term leach behavior of PGM is characterized by the absence of a significant pH excursion. As a result, the solubilities of the major glass components retain the low values typical of the neutral pH range, while species which tend to precipitate at high pH values such as Ca and Sr exhibit in this case a nearly congruent dissolution.

It has been concluded that the same leach mechanisms apply in the cases of TDS-131 and of PGM, but the high alkalinity of the former glass causes the corrosion of the matrix during immersion in water to be more extensive, especially at long contact times. Glasses such as DWRG with intermediate values of the

TABLE 1.19. Dynamic Leach Tests on PNL 76-68 Glass at 70°C

S/V, m^{-1}	T_r , days	pH	Leachate Concentration, mg/L						Normalized Leach Rates, $\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$					
			Si	B	Na	Sr	Cs	P	Si	B	Na	Sr	Cs	P
24	2	9.1	5.56	0.860	3.51	0.06	0.28	0.025	0.620	0.608	0.767	0.366	0.563	0.236
24	8	9.3	17.5	3.08	11.5	0.04	1.31	0.070	0.495	0.544	0.628	0.061	0.659	0.163
825	2	9.6	34.8	13.5	48.5	<0.01	1.74	0.319	0.113	0.278	0.308	<0.002	0.102	0.086
825	8	9.8	76.8	29.2	99.4	<0.01	2.55	0.480	0.062	0.150	0.158	<0.001	0.037	0.033
825	28	9.9	110	36.6	120	<0.01	2.73	0.912	0.025	0.054	<0.055	<0.001	0.011	0.018

TABLE 1.20. Dynamic Leach Tests on PGM Glass at 70°C

	PGM			
	24	825	24	825
S/V, m ⁻¹	24	825	24	825
T _r , days	28	28	28	28
pH	6.9	7.3	6.9	7.3
	Leachate Concentrations, mg/L		Normalized Leach Rates, g·m ⁻² ·d ⁻¹	
	24	825	24	825
Si	1.215	6.52	0.0068	0.0011
B	0.099	0.322	0.012	0.0011
Al	0.053	0.33	0.0018	0.0003
Na	0.18	0.72	0.012	0.0014
Ca	0.02	0.03	0.035	0.002
Sr	0.022	0.042	0.031	0.002
Cs	<0.01	<0.10	<0.009	<0.003
P	0.26	0.47	0.018	0.008

ratio between Na and Li on one hand and the buffering species Si and B on the other exhibit intermediate leach rates between the two extremes (DWS-131 and PGM) under all conditions. In order to verify the consistency of the trend further, leach tests were carried out on CUBS, a high-silica borosilicate glass (see Table 1.1) intermediate in composition between DWRG and PGM.^(a) CUBS contains almost as much SiO₂ as PGM, 56.9%, but its alkali oxide content is higher (5.4% Na₂O, 1.7% Li₂O). Other important constituents include 12.9% Fe₂O₃, 6.2% Al₂O₃, 4.9% B₂O₃ and 3.3% P₂O₅, with a resulting [Na+Li]/[Si+B] ratio of 0.26, exactly half-way between the corresponding ratios in the cases of DWRG and of PGM, respectively. The results of two flow tests carried out on CUBS and, in parallel, on DWRG are shown in Table 1.21. It can be seen that unlike PGM glass CUBS exhibits a pH rise above neutral upon leaching, although the rise is smaller by one pH unit than in the case of DWRG. Leachate concentrations of major glass components are 2 to 4 times lower in the case of CUBS than in the case of DWRG but higher by a similar factor than in the case of PGM. The studies on CUBS provide verification of the general trend towards better durability and corresponding smaller pH excursion in the

(a) Macedo, P. B., T. A. Litovitz, Aa. Barkatt, R. K. Mohr, C. J. Montrose and H. G. Sutter. "Improved Durability of Borosilicate Glasses for Nuclear Fixation." To be published.

TABLE 1.21. Dynamic Leach Tests on CUBS and DWRG Deionized Water, 70°C, S/V = 194 m⁻¹

Glass	DWRG	CUBS	DWRG	CUBS
T _r , days	28	28	112	112
pH	9.81	8.61	9.85	8.81
	Leachate Concentrations, mg/L			
	DWRG	CUBS	DWRG	CUBS
Si	26.8	12.8	37.9	23.0
B	3.88	1.03	5.48	1.90
Al	2.49	1.40	3.59	1.63
Na	8.74	1.76	14.3	3.79
Li	3.20	0.62	4.37	1.19
Cs	0.80	0.41	0.76	0.52
Ca	0.20	0.21	0.20	0.10
Sr	0.05	0.08	0.06	0.03
Fe	0.77	0.09	0.75	0.08
Mn	0.10	0.05	0.11	0.02
Ti	0.016	0.001	0.014	0.004
U	0.61	0.03	0.78	0.05

case of glasses with a relatively lower content of basic oxides.

1.6.3 Natural and Ancient Glass Analogs

A comprehensive discussion of observations on the extent of corrosion in natural and ancient glasses, which have been exposed for periods comparable to those of interest in geologic disposal of nuclear wastes, is beyond the scope of this chapter. However, it is encouraging to note that, in general, available data concerning the corrosion of such glasses tend to agree with, and thus to validate, conclusions based on short-term laboratory tests with regard to leach mechanisms, corrosion rates and surface structure. In agreement with the laboratory results detailed above, observations on hydrothermal leaching of rhyolite glasses in nature (Macedo, Barkatt and Simmons 1982) show that high-silica glasses, in contrast with low-silica borosilicate glasses, have high resistance to corrosion even under prolonged exposure in hydrothermal systems. Low-silica basaltic glasses (approximately 50% SiO₂) resist devitrification for long periods (10⁶ years) when dry, but upon exposure to water they exhibit rapid surface alteration and formation of clay-like rinds, typically about 0.1-mm thick, both in the field and in laboratory tests (Dickin 1981). Laboratory tests and field observations on

the corrosion of Australasian tektites show that although the hydration layer formed on their surface is extremely thin and matrix dissolution is the controlling leaching mechanism, land tektites have very low leach rates ($1.8 \times 10^{-5} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$), in agreement with their high silica content (70-79%) (Barkatt et al. 1984a). Extrapolations from laboratory tests based on linear corrosion (time-independent leach rates) agree extremely well with field observations. Although very durable, tektites corrode faster by a factor of 3 to 4 than man-made high-silica (94% to 95% SiO_2 , 5% B_2O_3 , 0.5% Cs_2O , <0.1% $\text{Na}_2\text{O} + \text{K}_2\text{O}$) glasses (Barkatt et al. 1984a). Microtektites with lower silica content have survived for very long periods as a result of their becoming rapidly surrounded by interstitial pore water which is highly saturated with respect to Si and Al (Allen 1982).

Dynamic leach tests on basalt and granite indicate the growing importance of several trends and mechanisms when increasingly long contact times are considered. These mechanisms include pH-dependent saturation with respect to silica, Al solubility control by aluminosilicate formation, selective leaching of soluble species such as Na^+ and Cl^- , and retardation of the leaching of di- and polyvalent cations (Mg, Fe) followed by overloading of the sorption capacity or stability of the surface (Glass and Crosbie 1981). It has been shown that these trends can be extrapolated to yield quantitative agreement with the observed composition of 2×10^4 -year old ground water obtained from basalt and granite formations (Glass and Crosbie 1981).

Studies of ancient glasses again give rise to conclusions which tend to confirm and validate extrapolations based on laboratory studies at increasingly long contact times. Glasses with high-silica content, particularly above 66.7 mol% (Barkatt et al. 1983), such as ancient Egyptian glasses, possess much higher durabilities than low-silica glasses, such as Roman and certain Medieval glasses. High-silica glasses tend to form upon weathering durable thin surface films, while low-silica glasses form powdery crusts, and this difference reflects the higher rate of matrix dissolution in the case of low-silica glasses (El-Shamy 1973). Selective leaching of soluble species such as alkalis (Kaplan and Mendel 1982) and surface enrichment with respect to di- and polyvalent metal ions such as Fe, Ca and Mg, (Peyches 1965), which follows their respective charge densities (Barkatt, Simmons and Macedo 1981), were observed in the cases of Roman and Medieval glasses as well as in the case of nuclear

waste glasses (Barkatt, Simmons and Macedo 1981). Medieval glasses with increasing alkali content and decreasing silica content develop surface films which are progressively less protective against further corrosion (Winter 1965). Crystalline alteration products have been observed to form on the exposed surfaces (Kaplan and Mendel 1982).

The finding that modern, ancient and natural glasses of similar composition exhibit similar leach behavior upon exposure to aqueous media has been generalized by Plodinec, Jantzen and Wicks (1984) to derive a general model for the dependence of corrosion rates of glass on their composition. Data obtained with all three types of glasses appear to give excellent agreement with the predictions of the model, covering a silica concentration range of roughly 30 to 80% (see 1.6.4).

1.6.4 Systematization of Glass Composition Effects

As detailed in Sections 1.5 and 1.6, it is not possible to obtain a general dependence of "durability" on glass composition since measured leach rates strongly depend on test conditions. For instance, it has been demonstrated that addition of alumina considerably improves the durability of glasses leached in neutral water, but greatly increases the rates of corrosion in both acid and alkaline media (Barkatt, Barkatt and Sousanpour 1982; Plodinec, Jantzen and Wicks 1984). Many systematic studies have been carried out on the effects of various glass components on the leach rates of ordinary (Morey 1954; Plodinec, Jantzen and Wicks, 1984) as well as nuclear waste glass (Soper et al. 1983; Ohta and Suzuki 1978; Nogues, Hench and Zarzycki 1982).^(a) However, most of these studies were carried out using either rapid-exchange tests or static tests, and in many cases S/V ratios and contact times were much lower than those expected under repository conditions. As a result, the most important mechanisms operating under repository conditions, viz. pH rise, saturation and alteration, are not fully reflected in many of the conclusions of these studies. For instance, Na_2O and B_2O_3 are sometimes considered together in analyzing compositional effects on durability (Ohta and Suzuki 1978). While this may be valid under neutral conditions, it was shown above (see Section 1.5 and Table 1.7) that at slow

(a) Also relevant: A. A. Hench and L. L. Hench. "Computer Analysis of Compositional Effects in Nuclear Waste Glass Leaching." Nucl. Chem. Waste Manage. In press.

flow rates durabilities are strongly affected by the ratio of basic oxides, in particular alkali oxides such as Na_2O , to acidic oxides such as B_2O_3 .

One conclusion which is widely supported by the experimental data is that long-term durability is primarily dependent on the composition and properties (chemical bonding, porosity, surface potential, sorption) of surface films formed during prolonged exposure to aqueous media (Yastrebova 1961; Hench 1977; Wallace and Wicks 1983; Barkatt, Simmons and Macedo 1981; Bates, Lam and Steindler 1983; Freeborn and White 1984). However, the surface structure itself is highly dependent on the conditions of exposure, in particular time, temperature and pH. This dependence can account at least in part for the ambiguity which exists in the literature concerning, for instance, the effect of iron oxides in glass (Van Iseghem, Timmermans and de Batist 1984). While replacement of iron oxides by alumina (Van Iseghem, Timmermans and de Batist 1984) or zinc^(a) improves the durability of nuclear waste glasses under highly diluted conditions and in the diffusion controlled stage by as much as a factor of 25, the differences under conditions of low dilution are much smaller according to Van Iseghem et al. (1984). Experiments carried out using different surface-to-volume ratios directly show large differences in surface structure and they indicate that in the solubility region iron is probably a major building block of a protective film (Wicks et al. 1982). The chemistry of iron alteration products, which may include hydroxides at high flow rates and silicates at low flow rates (see 1.5.9), may be responsible for some of these differences.

At the present time, extensive data on compositional effects on the durability of glasses are very limited (Ohta and Suzuki 1978). Existing data, mainly based on the tests described in Sections 1.5 and 1.6, indicate a major effect of the ratio of acidic to basic oxides. As detailed above, the improvement in glass durability upon raising the combined concentration of acidic oxides (SiO_2 , B_2O_3 , possibly P_2O_5) in the glass and the ratio between this concentration and that of alkali oxides is more noticeable at the lower flow rates.

Among general models proposed to account for compositional effects on glass durability, the hydration energy model (Plodinec, Jantzen

and Wicks 1984) has had significant success in the systematization of data based on short-term static tests. Since the acidity and basicity of the various glass components were not taken into consideration when this approach was first attempted, it is not surprising that the correlation between free energy of hydration and observed leach rates (based on silicon) shows large deviations in the case of nondurable glasses, which exhibit large pH excursions even in short-term tests. However, the model (which is described in further detail in Chapter 6) has been modified by Plodinec, Jantzen and Wicks (1984) to take into account the changes in pH and make suitable corrections based on the high-pH dissociation of silica and boric acids and the formation of silicate and borate ions. The use of the resulting modified model has yielded an impressive correlation between $\Delta G(\text{hydration})$ and the normalized loss of Si over a wide range of glass compositions, including modern, medieval and natural glasses. This indicates that attempts at systemization and generalization of compositional effects on glass durability can be fruitful and that both experimental and theoretical studies in this area should be pursued.

1.7 CONCLUSIONS

1.7.1 Total Exposure Time and Contact Time

The leach kinetics of nuclear waste glasses depend both on the total duration of the time during which the glass was exposed to water, t , and on the contact time, T_r , with a particular volume of leachant, i.e., the reciprocal of the leachant exchange rate. In other words, the leach rates, L_i , of the various glass components, i , can be described as $L_i = L_i(t, T_r)$. Let $f(t)$ describe the dependence on t . Thus $f(t)$ characterizes the change in the leach rate from the time the dry glass surface comes in contact with the leachant until it reaches steady state with respect to the aqueous phase. This factor dominates short-term hydration behavior, especially in static tests, but it is highly irreproducible, being dependent on the original surface roughness. At times relevant for geologic disposal steady state has already been reached, i.e., $f(t)$ becomes a constant, and L_i is described as a function of t_r alone. Since $f(t)$ often approximates the form t^α , where $\alpha < 0$, extrapolations based on short-term data can lead to low estimates of long-term leach rates. Relevant, conservative predictions of long-term values of L_i can only be derived from experiments carried out under conditions which follow $f(t)$ until

(a) G. G. Wicks. "Computer Study of International Waste Glasses." Unpublished.

it becomes constant. This makes it possible to isolate the steady-state dependence of L_i on T_r .

1.7.2 Dependence of Leach Behavior on Contact Time

When leach behavior is considered as a function of contact time or its reciprocal, the leachant exchange rate or equivalent flow rate, it is possible to conclude that at short contact times (rapid flow) the process is controlled by a constant leach rate and at long contact times (slow flow) by a constant leachate composition corresponding to solubilities of the components of the leached surface (Barkatt et al. 1983a; Hughes, Marples and Stoneham 1983). These two regions are bridged by a range of contact times with intermediate behavior. At extremely high flow rates leach rates may rise again due to corrosion-erosion effects (Winter 1965), although these are not very likely to occur under repository conditions. The lower limit of the region of slow flow rates is reached when the rate of diffusion of water throughout the repository site becomes comparable with the rate of actual mass flow (Barkatt et al. 1983a; Hughes, Marples and Stoneham 1983).

1.7.3 Effects of Glass and Leachant Composition

The controlling leach rates at the high flow-rate region L_i^0 , the controlling solubilities at low flow rates C_i^m , and the numerical values of the flow rates at which the transition between the two regions of leach behavior takes place are all affected by the composition of the glass. Glasses with high silica content and low concentrations of alkalis, for instance, tend to have lower values of L_i^0 and of C_i^m and to exhibit the transition to slow-flow behavior at relatively high flow rates. High-alkali glasses have high values of C_i^m and switch to saturation control only at very slow flow rates because of the exponential dependence of C_i^m on the pH and the large pH excursion which takes place upon leaching such glasses.

The effects of leachant composition on the leach kinetics can be attributed to the same factors, i.e., ground water leachants with a high Si content and moderate pH levels tend to produce saturation-controlled leach behavior at higher flow rates, except in cases when the glass is highly alkaline and its leaching produces a pH value which is significantly higher than the original pH level of the leachant.

1.7.4 Relative Leach Rates of Various Glass Components

The relative leachabilities of the various components of defense waste glasses are highly dependent upon the flow rate. Boron is invariably the most leachable species (Barkatt et al. 1983a; Wallace and Wicks 1983). At high flow rates the leach rates of the alkalis, Si and Al are similar to those of B, but at increasingly lower flow rates Al, followed by Cs, Si, Li and Na, becomes less leachable. The dissolution process at low flow rates probably remains nearly congruent, but under slow flow conditions the concentrations of many glass components reach saturation levels and solid products precipitate from the solution. Fe, Mn and Ni are not dissolved in the aqueous phase to a large extent under any conditions. Initially they contribute to the build-up of a gel layer on the glass surface, but they also form colloids which can lead to significant release rates at slow flow rates. The leach rates of the alkaline earths are extremely dependent on pH, and as a result they exhibit higher relative leachabilities, and even higher leachate concentrations, at high flow rates than at slow flow rates. Transition metal ions, lanthanides and actinides such as U are susceptible to complexation by Cl^- , F^- , SO_4^{2-} , CO_3^{2-} , etc., and they exhibit higher leach rates in ground water than in water with the same pH and a lower solute content.

1.7.5 The Role of the Surface Layer

Under all flow conditions, defense waste glasses exhibit a rapid modification of the surface due to hydration during the first few days of contact with aqueous media. However, in the long term the modified surface does not function as a leach-controlling diffusion barrier, and within a few days matrix corrosion begins to control the leach rates. At high flow rates the ensuing dissolution is almost completely congruent and linear with time, as only minor components (Fe, Mn and Ni) stay undissolved to a large extent, apparently forming a porous low-density gel layer which does not have a very significant effect on the kinetics. At lower flow rates the fraction of Si, the major component of the glass matrix, which passes into the solution becomes increasingly smaller. The same is true for Al. Under slow-flow conditions the solubility of Si and Al becomes controlled by the formation of more stable alteration products [possible species may include silica crystallized as quartz or cristobalite or hydrated silica (Spychalski 1983), and various silicates such as analcime, acmite, weberite, tobermorite and

montmorillonite - cf. Chapter 2)]. These alteration products have lower solubilities than the original glass and thus they control the rates of loss of the major components of the glass matrix, Si and Al, at low levels. (These rates are determined in the saturation region by the product of the solubility and the rate of leachant exchange.) The concentrations of soluble glass components (e.g., boron and alkalis) in the leachates under slow-flow conditions level off at values which are somewhat higher than the concentration of silica (normalized by the relative abundances in the original glass composition) but are very low relative to their solubility limits. This indicates that the alteration process gives rise to the formation of a highly effective protective layer which is impermeable or nearly impermeable with respect to the migration of all glass components.

When this layer reaches a certain depth the processes of depletion and alteration of the residual original glass can only proceed further at a rate which is determined by the removal of dissolved silica caused by the replacement of the water in contact with the glass due to flow. In summary, both solubilities and protective layer build-up and structure are important in determining the release rates of the various components of glassy waste forms under slow-flow conditions which are likely to prevail in actual service.

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CHAPTER 2

SURFACE LAYERS IN LEACHED BOROSILICATE GLASS HIGH-LEVEL DEFENSE NUCLEAR WASTE FORMS

CHAPTER 2

Surface Layers in Leached Borosilicate Glass High-Level Defense Nuclear Waste Forms

ASSIGNMENT: MEASURE THE PHYSICAL AND CHEMICAL PROPERTIES OF THE SURFACE LAYERS FORMED AS A RESULT OF LEACHING OF BOROSILICATE WASTE GLASSES TO PROVIDE MECHANISTIC INFORMATION ON THE PROCESSES INVOLVED.

SUMMARY: Dehydrated surface layers on leached glass samples were examined by electron microscopy and analytical spectroscopic techniques to observe their morphology, chemical composition and crystallinity. Comparison of SEM/EDS, SIMS, EDXS and XPS chemical depth profiles and physical layer thickness data with solution concentration measurements yielded good agreement, supporting the validity of observations made on dehydrated layers. Pertinent features observed in the surface layers are illustrated below:

The interface between the altered layer and the bulk glass was observed to be physically and chemically well defined, except for a narrow (<1 micron) imperfectly characterized reaction zone in the glass below the alteration layers in which depletion of only the most soluble elements (B, Li, Na) could be measured. The sharp boundary between the alteration layers and the bulk glass, the marked elemental distributions within the alteration layers, and the well-defined physical features of the alteration region indicate that its properties are directly affected by reactions with the aqueous environment and are not simply the result of incongruent dissolution of the glass matrix. Dilute leachants produce thick, low-density surface layers. Concentrated leachants characteristic of low-flow or static experiments (and silicate ground waters) produce thin, higher-density surface layers. The presence of metallic Fe in oxygenated leaching environments accelerates the dissolution process through iron-silicate reactions, producing alteration layers dominated by Fe chemistry.

Reaction products forming in and on the alteration layers in testing at 90°C and below are consistent with those found in hydrothermal leaching studies and with observations made on analogous natural geochemical systems.

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CHAPTER 2.0

SURFACE LAYERS IN LEACHED BOROSILICATE GLASS HIGH-LEVEL DEFENSE NUCLEAR WASTE FORMS

SYNOPSIS

Borosilicate glass waste forms begin to react immediately when exposed to an aqueous environment. This process, whose rate and mechanism are a strong function of both the glass composition and environmental parameters, produces alteration layers at the exposed glass surface. The morphology, chemical composition, and rate of formation of these alteration layers provide insight into the long-term dissolution processes which such glass forms would be expected to undergo in a geologic repository. This section deals with results of the analysis of alteration layers and other solid products of the reactions of borosilicate waste glasses with aqueous environments. The primary techniques used in this portion of the experimental program were scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDXS) combined with such surface spectroscopic techniques as x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), sputter-induced photon spectroscopy (SIPS), and scanning Auger microscopy (AES, SAM). Phase identification work relied primarily upon powder x-ray diffraction (XRD). The principles of these techniques and their application to the analysis of alteration layers in nuclear waste forms have been summarized elsewhere (Mendel and Harker 1983).

2.1. PHYSICAL CHARACTERISTICS OF WASTE GLASS ALTERATION LAYERS

The morphology of the alteration layers in leached vitreous waste forms is dependent upon the physical and chemical processes controlling their formation. The alteration layers are highly structured, with their initial gross morphology dependent upon the bulk glass surface condition. The microstructure of the alteration layers, however, tends to be very similar under all conditions. Figure 2.1 shows SEM micrographs of the leach layer formed on the defense waste reference glass (DWRG) after 28 days of MCC-1 static testing at 90°C in deionized (DI) water. The honeycomb appearance is a common

feature of the layers, though their thickness and chemical composition may differ considerably. The open porosity of the leached layers is indicative of their low density, which varies from about 0.8 to 2 g/cm³, depending upon the leaching conditions. Flowing tests or highly dilute static deionized water tests produce the less dense alteration layers, and silicate water or high SA/V tests produce the more dense.

Figure 2.2 shows SEM views of a leached layer formed in 209 days of static deionized water leaching of a thermally cracked sample of the DWRG which was subjected to no surface re-finishing. The alteration region breaks into two well defined layers and separates cleanly from the bulk glass. The upper layer has the familiar open porosity of Figure 2.1, while the lower layer appears more dense. This suggests a graded density, with the inner gel having the more closed porosity. The altered glass surface and the underside of the alteration layer show well ordered connected pits, which appear to follow parallel stress lines in the glass.

Layered structuring of the alteration region is common, with layers typically having thicknesses of 0.5 to 2 microns. Fractured samples and highly polished surfaces tend to exhibit stacked flat layers. This can be seen in Figure 2.3, which shows an edge view of six separate stacked layers in the alteration zone on a 600-grit-polished sample of TDS-131 glass which was exposed to a 50 cm³/h flow of deionized water at 90°C for 14 days at the University of Florida. In contrast, Figure 2.4 shows a 30-micron-thick alteration zone separated from a DWRG sample after 183 days of 90°C IAEA-type deionized water replacement testing at Catholic University. The original glass surface had the equivalent of a 360-grit polish with scratches still visible. The alteration zone shows 12 to 20 clearly distinguishable, highly convoluted layers. The variations in contrast and texture visible in the SEM micrograph again suggest density gradients in the layers. In this case the layers in the center of the

FIGURE 2.1. SEM Micrographs of the Alteration Layers Formed on 3-Micron-Grit-Polished DWRG in 28 Days of Deionized Water Leaching at 90°C Under MCC-1 Conditions

ALTERATION LAYERS, 2000 x

OUTER SURFACE, 5000 x

BOTTOM SURFACE OF OUTER LAYER,
5000 x

FIGURE 2.2. Seven SEM Views of Two Alteration Layers Formed on a Sample of the As-Cast DWRG with a Thermal Fracture Surface. Leach conditions: 209 days, deionized water, 90°C, SA/V = 10 to 20 m⁻¹.

UPPER SURFACE OF INNER ALTERATION LAYER
MAGNIFICATION - 5000 x

BOTTOM SURFACE OF INNER ALTERATION LAYER
MAGNIFICATION - 2000 x

BOTTOM SURFACE OF INNER ALTERATION LAYER
MAGNIFICATION - 5000 x

LEACHED GLASS SURFACE
MAGNIFICATION - 2000 x

FIGURE 2.2. (contd)

FIGURE 2.3. Six Alteration Layers Formed on a Sample of TDS-131 Glass During Flow Test Leaching at the University of Florida. Conditions: 50 cm³/h, deionized water, 90°C, 600 grit surface polish.

convolutions appear more dense than the outer layers, both top and bottom. The underside of this leached material has a washboard-like morphology, with tubular-appearing configurations that conform to the convolutions in the inner layers. This interesting morphology is characteristic of thick alteration zones formed under dilute leaching conditions (low SA/V) on waste glass samples that have diamond sawed or coarse polished surfaces (Harker and Clarke 1982).

It is significant that the leached layers appear to quantitatively retain the original dimensions of the waste form. The only observed deviations from this have been caused by precipitate buildup or by the leach layers sloughing off the samples. Evidence of this comes from a self-consistent calculation of the effective elemental depletion depth into the original glass surface based upon solution concentrations and elemental ratios observed in the alteration layers by EDXS. The effective leaching depth of species *i*, T_i , can be approximated by iteratively solving expression 2.1 in which the total amount of an element observed in solution, TDS_i , and in the alteration layer is divided by the amount of that element in the bulk glass and the geometric sample surface area.

$$T_i = (TDS_i + F_{li}P_lV_l)/F_{gi}P_gSA \quad (2.1)$$

where:

P_l = alteration layer density

P_g = glass density (2.7 g/cm³)

F_{li} = average fraction of species *i* in the layer

F_{gi} = fraction of species *i* in the glass

V_l = volume of alteration layer

SA = surface area of sample.

In solving the expression the initial alteration layer thickness is taken from the SEM observation. The calculated value for T_i is then iteratively substituted back into the equation until a self-consistent effective layer depth is reached. Table 2.1 shows such a comparison for the DWRG alteration layer shown in Figure 2.4. The excellent correspondence between the solution and depth profile measurements confirms that the alteration zone retains the original dimensions of the glass sample under the low SA/V conditions of IAEA-type testing. Static and slow flow tests show similar results, altered only by the presence of precipitates.

A similar approach was used to estimate the density of the alteration layers under a variety of leaching conditions. By assuming that the total boron release gives a measure of the depth of glass leaching and summing the total dissolved solids released from the glass, an approximate layer density can be calculated based on the geometry of the form and the amount of glass species remaining in the altered volume as given in equation 2.2.

$$P_l = (P_gV_l - TDS)/V_l \quad (2.2)$$

The results of plotting the estimated layer densities versus flow rate for a number of leaching tests conducted at Catholic University are shown in Figure 2.5. The estimated density can be seen to increase monotonically with decreasing flow rate for deionized water experiments, and to reach levels of about 2 g/cm³ in silicate water tests at low flow. The presence of ductile iron in the air-saturated leach tests produced a greater variability, but in general tended to increase the estimated densities under all flow conditions, presumably due to increased precipitation biasing the calculation. Physical measurements on dehydrated alteration layers formed in the presence of Fe yielded densities between 1.5 and 2.0 g/cm³. These dehydrated layers were found to be enriched in Fe and Si with respect to layers produced under similar conditions without metal present.

OUTER SURFACE - 300 x

EDGE VIEW - 1000 x

INNER SURFACE - 300 x

FIGURE 2.4. Three SEM Micrographs of the 30-Micron-Thick Alteration Zone Formed on a 360-Grit-Polished DWRG Sample in 183 Days of Water Exchange Testing at Catholic University. Conditions: deionized water, 25% volume water exchange at intervals from 1 to 30 days, 90°C, SA/V = 7 m⁻¹.

Table 2.1. Comparison of Calculated Elemental Leach Depths, from Solution and Gel Layer (EDXS) Concentration Data, with Those Observed by SEM/EDXS in a DWRG Alteration Region Produced in 183 Days of IAEA-Type Testing in Deionized Water at 90°C

Element	Calculated ^(a) Layer Thickness, microns	SEM/EDXS-Based Layer Thickness, microns
Li	36.8	No data
B	31.9	No data
Na	35	35 to 40
Al	35	32 to 35
Si	31	30
Ca	31	32
Fe	28 to 32	30
Cs	43	No data
U	44	30 to 32

(a) In the calculation a measured average dehydrated density of 1.1 g/cm³ was used for the alteration layers.

2.1.1 Cracking and Surface Roughening

Surface cracking and roughness play a strong role in establishing the morphology of the alteration layers. Typical diamond sawed samples have a rough surface with considerable cracking, which appears to accelerate initial layer formation. Figure 2.6 shows SEM micrographs of the fracture edges of DWRG samples, prepared with various surface finishes, after 28 days of 90°C static DI water leaching. The effect of surface roughness is quite apparent. The 3-micron polish produces a fairly uniform, submicron-thick leach layer with scattered pitting. The 400- and 600-grit-polished surfaces have rugged layers showing enhanced pitting and cracking, with thicknesses of >5 microns. Water penetration into surface cracks is visible in the micrographs, which show the alteration process in the cracks to progress at the same enhanced rate as observed on the roughened surface. Further studies of cracks, produced by indent fractures, confirmed that even

FIGURE 2.5. Plot of Calculated Alteration Layer Densities on Leached DWRG Surfaces as a Function of Flow Rate of Deionized and Simulated Groundwaters. The data were taken from water replacement test at Catholic University with effective flow rate calculated at a normalized SA/V x t value.

3 μ DIAMOND

600 GRIT POWDER

400 GRIT PAPER

MAG 2000 x

FIGURE 2.6. SEM Micrographs of the Alteration Layers Produced on Samples of the DWRG in 28 Days of MCC-1 Type Testing in Deionized Water at 90°C as a Function of Surface Finish

microscopic cracks are susceptible to water penetration (Harker and Clarke 1982). The leached zones in the cracks differ from surface alteration layers primarily in the distribution of transition elements, which migrate to the center of the alteration region within the crack.

It is expected that the bulk of the exposed glass surface in an actual form will be that produced by thermal stress cracking. This stress cracking produces a stepped surface with the regions between cracks having a finish equivalent to about a 3-micron grit polish, and it has been demonstrated that

crushed samples (48 to 100 mesh) waste glass leach similarly to polished monoliths after residual fines have been washed away or have reacted (Macedo et al. 1983). However, the alignment of the observed glass corrosion pits (Figure 2.2) and studies of stressed glass hydration (Bates, Steindler and McDaniel 1984) do indicate that the thermal stress lines act as centers for increased reactivity. These results indicate that kinetic studies must take great care in surface preparation, and that actual fracture samples may provide the best simulation of waste form performance.

2.1.2 Pitting

Removal of the leach layers from the bulk glass leaves a mirror image of the alteration zone subsurface. As shown by the SEM micrographs in Figure 2.7, these leached surfaces exhibit varying degrees of pitting. The samples of DWRG in the figure show that the degree of pitting increases with both the severity of the leaching environment and the duration of the test. However, by far the greatest effect is associated with the surface finish. The 600-grit-polished sample has much more severe pitting than a comparable 3-micron-grit-polished specimen, and the pits themselves show orientation effects from the 600-grit finish. This argues that the pitting is associated with microscopic imperfections or nonuniformities in the glass associated with its production and surface finish. This is supported by the uniform connected pit rows shown in the SEM micrograph of the thermally cracked sample, Figure 2.2. The parallel rows of pits on the cracked glass surface are obviously related to a regularity in the glass physical structure, most probably stress lines.

There is also evidence that surface precipitation increases the extent of the pitting either through localized effects or through a general enhancement of the leaching process. Figure 2.8 shows SEM micrographs of the top and bottom surfaces of a DWRG sample suspended horizontally in a static 90°C leach test with deionized water and an equal surface area of the reference canister metal. The upper surface collected a thick layer of settled precipitates, while the lower surface showed only scattered reaction product growth. Removal of the alteration zone showed that the upper surface had experienced about twice as much pitting as the lower surface.

As the leaching process progresses the pits in the glass overlap and form connected patterns in the leach layer. These chain-like

structures in the sublayers of the alteration zone are probably the precursors to the washboard-like convolutions observed in extensively leached samples (Figures 2.2 and 2.4). A major effect resulting from the pitting process is that the surface of glass exposed to the leach solution is increased with time, which will affect any kinetic modeling of the system.

The physical origin of the pitting phenomena is still under investigation. The similarity in size and shape of the pits indicates that they may be forming under thermodynamic control and may be modeled by "etch-pitting" theory (Ives 1974). Though localized theories have been primarily developed for crystalline materials, the basic assumption that the point of origin of every pit is at a center of weak molecular attachments describes the observed dependence of the pitting process in the waste glass upon surface condition. In addition, the most simple theories for pit formation in a perfect surface rely upon the basic parameters of dissolution models: solubilities and the chemical potential for dissolution. The formation of etch pits has been modeled by both heterogeneous and homogeneous nucleation theory, and the application of these models to the observed pits in the waste glasses under various conditions potentially offers another tool for describing the thermodynamic driving forces in the dissolution process.

2.1.3 Precipitates

Another major physical feature of leached waste glass is the formation and deposition of reaction products at the outer surface. In low flow and static testing, where precipitation, crystallization, and complex formation are enhanced, the outer surfaces of the leached glasses show a variety of structures which do not conform to the original geometric dimensions. The formation of reaction products is greatly enhanced by the Si-Fe reactions occurring in the presence of the reference canister metal (RCM) in deionized water (McVay and Buckwalter 1983). Figure 2.9 shows the outer surface of matched samples of the DWRG leached for 143 days at 90°C in static deionized water, with and without an equal surface area of the RCM. The DWRG control sample shows scattered light precipitates and some geometric patterns in the dehydrated surface, perhaps indicative of crystallization. The DWRG + RCM experiment, however, produced a large quantity of flocculent amorphous material in the solution as well as nodular precipitates and well formed star-shaped crystallites, identified as maghemite or magnetite. Comparison of top and

**DEIONIZED WATER, 28 DAYS
3 MICRON POLISH, 200 x**

**DEIONIZED WATER, 28 DAYS
600 GRIT POLISH, 200 x**

**DEIONIZED WATER, 143 DAYS
200 x**

**DEIONIZED WATER + CANISTER
METAL, 7 DAYS, 200 x**

FIGURE 2.7. SEM Micrographs Showing Pitting of the DWRG Beneath the Alteration Layer, Produced During Static Leaching Under Various Conditions

TOP SURFACE OF DWRG, 2000 x

BOTTOM SURFACE OF DWRG,
2000 x

TOP LEACHED GLASS SURFACE
200 x

BOTTOM LEACHED GLASS
SURFACE, 200 x

FIGURE 2.8. SEM Micrographs Demonstrating the Effects of Precipitate Deposition on the Extent of Pitting of the DWRG Surface During Leaching. Conditions: 7 days MCC-1 leaching at 90°C in deionized water with an equal surface area of the reference canister metal and DWRG.

DWRG + STATIC DI WATER

DWRG + RCM + STATIC DI WATER

FIGURE 2.9. SEM Comparison of Surface Precipitate Formation on the DWRG in Deionized Water at 90°C With and Without the Reference Canister Metal Present After 143 Days of Static Leaching Under MCC-1 Conditions.

bottom views of the DWRG in the interactive experiment showed that much of the flocculent material was deposited on the glass surface by settling, which indicates that it was formed in solution. The light-contrast, nodular precipitates were present on both top and bottom glass surfaces in roughly the same quantity and are attributed to reactions occurring at the glass surface.

In the 143-day static interactional test in deionized water, the samples of canister material showed significant surface corrosion; however, it was interesting to note that areas of the metal were unaffected by the water exposure, retaining their initial polish. The SEM micrograph in Figure 2.10 confirms that the same types of Fe-containing precipitates (star-shaped crystals of magnetite or magnetite) are present on the canister metal surfaces as were observed on the glass. The light-colored nodular precipitates were not present on the metal surface, which argues for the preferential formation of these precipitates at the glass surface.

The presence of uncorroded zones on the canister metal samples in deionized water testing and the observation of retardation of the metal corrosion process in deoxygenated silicate water emphasize the strong dependence of the metal-glass interactions on water Eh, pH, and cation content. The chemistry of these

interactions will be discussed in more detail in section 2.3.

2.1.4 Alteration Layer Formation Rates

As long as saturation has not been reached with respect to the highly soluble elements, the rate of penetration of the leach solution into the bulk glass can be approximated by solution measurements of boron and lithium release as a function of time, or by SEM observation of physical layer thickness. Comparison of these two techniques has shown excellent agreement (Harker and Flintoff 1984). Figure 2.11 compares alteration layer thickness as a function of time of exposure to deionized water for samples of the DWRG prepared with both 600-grit and 3-micron finishes. The static tests were run at 90°C and at a SA/V ratio of 20 to 50 m⁻¹. The monotonic growth of the layers shows a significant effect of surface roughness that continues throughout the time of the test. The filled triangles, labeled "cracked," indicate the layer thickness observed under similar conditions with samples of thermally cracked DWRG (Figure 2.2) with no surface preparation. The cracked glass samples had alteration layer thicknesses similar to those observed for the 3-micron polished samples. Any change in the conditions of the tests alters the observed rate of layer formation.

FIGURE 2.10. SEM Micrographs of the Precipitates Formed on the Reference Canister Metal in Deionized Water Leaching with the DWRG at 90°C After 143 Days

FIGURE 2.11. Growth of the Alteration Zone on Samples of the DWRG as a Function of Time of Exposure to Deionized Water at 90°C Under MCC-1 Conditions (except where noted). Several conditions and surface finishes are represented. Open circles = TDS-131, 0.5 cm³/h flow DI water; closed circles = 3-micron polished samples of DWRG (MCC-1); squares = DWRG with 600-grit polish (MCC-1); diamonds = DWRG with 3-micron polish + an equal surface area of RCM (MCC-1); triangles = thermally cracked sample of as-cast DWRG (MCC-1). The arrows indicate that portions of the layers were significantly thicker; the dashed lines show the regions bound by the uncertainty in the measurements.

Using less stable glass such as the TDS-131 or going to flowing conditions greatly enhances the layer formation rate, while using a silicate ground water slows the alteration process. As examples, discrete data points are included in the figure to show observed layer depths with TDS-131 glass leached at a 0.5 cm³/h flow rate of deionized water after 28 days and to demonstrate the effect of including the reference canister metal in the static DWRG leach tests. This significant dependence of glass alteration layer formation rate upon surface morphology can be a dominant effect in many laboratory leaching experiments and must be considered in data interpretation.

2.1.5 Summary

From these laboratory observations a physical picture of the alteration layers produced by leaching of a glass waste form can be developed. The contact of water with the glass surface initiates the layer formation by leaching away the soluble cations, leaving a skeletal structure of the original form which retains the initial geometric dimensions. The growth of the alteration layer proceeds into the glass with cracks and microscale roughness accelerating the process (as much as an order of magnitude). Pit formation in the altered glass surface is common, with pits preferentially appearing on stress lines and in areas of surface disruption. The physical and chemical processes involved produce distinct layering in the alteration zone with polished or smooth cracked surfaces having the more uniform layers. On roughened or poorly polished glass surfaces the alteration region still forms in well defined layers, but the layers themselves are highly convoluted. In all cases the alteration layers have good integrity and have a well defined boundary with the bulk glass.

The presence of reactive solids such as canister metal in the leach system, with initially air saturated deionized water, significantly accelerates the removal of silica from the glass and leads to the formation of colloidal complexes and well-defined crystalline precipitates on the glass surface. Small node-like and flocculent precipitates are common in all systems where water flow is low enough for saturation to occur. Some crystallization of the alteration layer may be occurring.

2.2 CHEMICAL COMPOSITION OF ALTERATION LAYERS

The alteration layers in leached borosilicate glasses have common features in that they are formed primarily by the removal of the more

soluble elements and the migration and reaction of the remaining species, but their chemical and phase composition depend highly upon the solution species present in the water, Eh, pH, canister metal, rock, etc. The altered glass is a hydrous transition metal and silica-rich material, whose density appears to be dependent upon the extent of Si leaching in the alkali and B depleted zone. Much of the elemental distribution in the alteration layers is associated with the migration of the remaining species to the solution and glass interfaces. The outer surface of the layers is the preferred location for precipitation of amorphous and crystalline solid phases. The amorphous precipitates can act as precursors to further crystalline phase formation and as adsorption sites for actinides. Studies have indicated that the chemical composition of the alteration layers may have a significant effect on the long-term leach rates by establishing a low chemical potential difference between species in the layers and the glass, thus reducing the overall driving force for dissolution (Grambow and Strachan 1983).

2.2.1 Chemical Composition in the Early Stages of Dissolution

The early stages of surface layer formation were examined using sputter-induced photon spectroscopy (SIPS) and secondary ion mass spectroscopy (SIMS) (Houser and Pantano 1984). The experiments were carried out on three different glasses: DWRG, TDS-131, and PNL 76-68. The glasses were leached at two different surface area-to-volume ratios (SA/V). According to the formulation developed by Macedo et al. (1983) the product of SA/V and leaching time is a scaling factor. Thus, at very low SA/V (0.1 m² in this case), the very early stages of film growth can be observed and used to rationalize the more complex film structures observed at higher SA/V (10 m² in this case) or at longer times (e.g. the SEM analyses performed on layers formed at longer leach times).

In general, these depth profiling analyses cannot be used for quantitative compositional determinations within the layer because of the unknown density and matrix effects of the layer. Nevertheless, a semi-quantitative description of the leach layer composition and composition differences among various glasses can be achieved. On the other hand, the thickness and growth rate of these very thin films can be determined in a quantitative way. The rates of surface layer growth for polished surfaces under MCC-1 static leach conditions in DI water were 0.02, 0.07, and 0.14 micron/d for DWRG, TDS-131, and PNL 76-68, respectively. The rates were obtained

from SIPS depth profiles with depths calibrated by surface profilometry, on glasses leached for 1, 3, 7, 14, and 28 days. These values correlate well with those observed at longer times by SEM (see Figure 2.11).

Figures 2.12, 2.13, and 2.14 compare the SIPS depth profiles for the DWRG under various conditions at 90°C in deionized water. Due to the variable density of the surface layer(s) it is not possible to compare the signal levels between the surface and bulk for even semi-quantitative analysis. Nonetheless, the presence, extent, and chemical composition of the surface layer(s) can be determined. The boron and sodium profiles are the best indicators of the overall reaction depth. It is noteworthy that except for the earliest stages of the reaction (Figure 2.12), the boundary between the surface layer and bulk is extremely sharp (Figures 2.13 and 2.14). This suggests that the glass dissolution is congruent. In fact, depth profiles were measured at regions where the surface layer flaked off and these profiles were identical to those of freshly polished samples. Thus, the glass dissolution process is not mediated by a diffusion-limited reaction at the interface between the bulk glass and reaction front in these experiments.

FIGURE 2.12. SIPS Depth Profiles for Polished DWRG After 100 Hours in Deionized Water at 90°C at SA/V = 0.1 m⁻¹. At the earliest stages, congruent dissolution of the DWRG depletes all elements except Si and B in the surface film.

FIGURE 2.13. SIPS Depth Profiles for Polished DWRG After 28 Days in Deionized Water at 90°C at SA/V = 0.1 m⁻¹. At this stage of dissolution the surface film shows the formation of a layer of hydrated Fe formed either by adsorption or precipitation.

Figure 2.12 represents the earliest stages of film formation. Here, the shallow penetration of H, and the depletion of all constituents except Si and B, can be observed. It may be significant that the other glasses examined (TDS-131 and PNL 76-68) underwent a complete loss of B under these conditions. The profiles in Figure 2.13 represent a later stage of the film formation where the adsorption or precipitation of iron or iron hydrates has been initiated at the glass-water interface. Figure 2.14 shows a much later stage of the reaction. The advancing reaction front has produced an insoluble hydrated iron-silicate film due to the congruent breakdown of the glass structure and the migration of the soluble species into solution. At the same time, an outer layer has begun to form due to adsorption or precipitation of hydrated magnesium and aluminum oxides at the hydrated iron silicate film-water interface.

In general, it appears that as solubility limits for each of the metastable hydrates are achieved in solution, their adsorption is initiated at the water-glass interface. It is likely that the negative charge associated with the silica surface enhances the adsorption of positively charged iron and and aluminum hydrates at the surface.

FIGURE 2.14. SIMS Depth Profiles for Polished DWRG After 100 Hours in Deionized Water at 90°C at SA/V = 10 m⁻¹. Later in the dissolution process an outer layer is formed in the alteration zone as hydrated Mg and Mn precipitate or adsorb at the water-glass interface.

Subsequently, these insoluble hydrates concentrate within the alteration layer as the reaction front moves into the glass. This hydrated surface layer is undoubtedly a porous, permeable membrane through which soluble species can migrate into the solution. Of course, many of these soluble species may be adsorbed during their out-migration, and will thus also be concentrated in the surface layers. The extent of adsorption will be determined by the isotherm which relates the quantity of species adsorbed to its concentration in the liquid phase.

The SIMS profiles in Figure 2.15 show the incorporation of the minor constituents within the hydrated iron-silicate film on TDS-131 after 28 days in deionized water at a SA/V ratio of 10 m⁻¹. The concentration of Sr and Ca within the surface layer (just behind the moving front) is clearly evident. At the same time, the precipitation or adsorption of Mg and Mn has occurred from solution at the surface-water interface.

The data of Figures 2.12 through 2.15, taken together, indicate the following sequence of initial film growth:

- 1) formation of a narrow, transient inter-diffusion zone due to preferential release of most constituents, except SiO₂ and some of the B₂O₃, to a depth on the order of 100 to 500 angstroms, depending upon the local Fe concentration in solution
- 2) growth of an iron-silicate film (inner layer) until the local solution concentrations of Al, Mg, and Ca reach saturation
- 3) precipitation and/or growth (possibly due to adsorption within the iron-silicate film) of an outer-layer consisting of Al, Ca, and Mg hydrates.

Clearly, the formation of multiple layers is a general feature of the glass dissolution process. The chemical composition of the layers depends upon the sequential attainment of solubility limits in solution, the adsorption or precipitation of insoluble hydrates at the surface-water interface, and sequential incorporation of these insoluble hydrates behind the advancing reaction front.

Interestingly, the general features of these surface layers, and the sequence in which they form, are qualitatively identical for the three glasses examined. That is, the Fe-hydrates are the first species to concentrate at the glass-water interface after an initial period of preferential leaching. Subsequently, a second outer layer rich in Al and Mg forms. The duplex structure of these layers is especially evident in the SIMS profiles for TDS-131 (Figure 2.15). Nevertheless, there are some unique features of these other glasses (relative to the DWRG) which are worth noting. During the initial preferential leaching period, these glasses release virtually all of the B in the surface layers, whereas a finite (although unknown) quantity of B was retained in the silica-rich film of the DWRG. This suggests that the structural incorporation of B in the DWRG may be different than that in the TDS-131 and PNL 76-68 glasses. This may be one factor in reducing the overall reaction rate of the DWRG relative to the other glasses. In addition, the distribution of insoluble hydrates between the inner and outer layers is slightly different. Neither the TDS-131 or PNL 76-68 glasses show a build-up of Ca at the outer layer, although the TDS-131 shows a rather substantial concentration of Ca in the inner layer. The TDS-131 glass also shows concentrations of Cs and Sr within the inner layer.

FIGURE 2.15 A AND B. SIMS Depth Profiles for Polished TDS-131 Glass After 28 Days at 90°C in Deionized Water at SA/V = 10 m⁻¹. The profiles show the multiple layer structure of the elemental distribution in the alteration zone. Ca and Sr are enriched in the inner layer.

2.2.2 Chemical Effects in Alteration Layer Development

The major elements in the DWRG alteration layers are Si, Fe, Al, Mn, Ni, Ca, and Mg. The soluble bulk species in the glass (Na, B, Li) are generally depleted in the alteration region. A key feature of the composition of the altered glass is the ratio of Si to the other elements. Aggressive leaching conditions in which precipitation reactions do not stabilize the leached layers result in a depletion of the Si in the alteration region. This is accompanied by continuing high leach rates of the bulk glass. In systems where saturation with respect to solid silicates in the alteration zone is approached, precipitation can occur which move the system toward steady state and stabilize the Si in the leach layers. In these cases the layers are thinner and alteration of the bulk glass progresses at a much reduced rate (Chapter 1; Grambow and Strachan 1983).

The controlling nature of silica in the system is apparent when the composition and thickness of alteration layers formed in different aqueous environments are compared as in Table 2.2. The four static test sys-

tems, using 600-grit-polished samples of the DWRG, show the stabilizing effects of silicate ground water and the aggressive reactions of Fe metal in initially air-saturated solutions. The Si content of the thinner layers is higher and drops monotonically as the leaching conditions become more aggressive and the leached layers thicker.

The relative Si content in leach layers also provides information on the stability of the glass in the leaching environment. Figure 2.16 shows SEM micrographs of two samples of the DWRG leached in the same container under MCC-1 conditions in deionized water at 90°C for 270 days. Both samples were originally polished to a 3-micron finish, then one was scratched with one pass on 600 grit paper. The control sample has a uniform 1-micron-thick alteration layer. The scratched sample has been leached irregularly to an average depth of about 3 microns, with the leach zone penetrating into the cracks to greater depths. The EDXS analyses of the two alteration zones in Table 2.3 show the polished sample to have a significantly higher Si content. This indicates that the surface roughening process disrupts, either physically or thermally, the structural

TABLE 2.2. SEM/EDXS Comparison of Alteration Layer Thickness and Chemical Composition on 600-Grit-Polished DWRG Monoliths Exposed to Different Static Leaching Environments at the University of Florida. Atomic ratios were determined by quantitative EDXS using DWRG and pure phase nepheline reference standards, with the experimental uncertainty estimated at 10%.

Case 1. MCC-1 testing at 90°C in silicate ground water for 28 days.

Case 2. MCC-1 testing at 90°C in deionized water for 28 days.

Case 3. MCC-1 testing at 90°C in silicate ground water with canister metal present for 28 days.

Case 4. MCC-1 testing at 90°C in deionized water with canister metal present for 28 days.

Layer Thickness

Case 1. 0.35 ± 0.1 microns

Case 3. 1.0 ± 0.2 microns

Case 2. 0.50 ± 0.1

Case 4. 0.9 ± 0.2

Normalized Layer Elemental Composition, Ratioed (atom basis) to Si

	Si	Al	Ca	Mn	Fe	Ni	U	Si/Total (%)
Case 1	1.0	0.21	0.07	0.17	0.46	0.16	0.01	48.1
Case 2	1.0	0.39	0.11	0.25	0.94	0.15	0.08	34.2
Case 3	1.0	0.30	0.04	0.49	2.20	0.38	0.08	22.3
Case 4	1.0	0.33	0.14	0.68	2.30	0.48	0.11	19.8

3 MICRON POLISH - 2000 x

SCRATCHED SURFACE - 5000 x

FIGURE 2.16. SEM Micrographs of the Alteration Zones Forming on Two Samples of DWRG After 270 Days of Static MCC-1 Testing at 90°C in Deionized Water. One sample had a 3-micron finish; the second was polished to a 3-micron finish, then scratched with 600 grit paper.

TABLE 2.3. Elemental Ratios Observed by Quantitative EDXS in Alteration Layers Produced by 270 Days of Static Deionized Water MCC-1 Leach Testing at 90°C on Two Samples of the DWRG (estimated uncertainty 10%)

Case 1. 3-micron polish, leached layer 1.0 ± 0.1 micron thick.

Case 2. 600 grit scratches on 3-micron finish, leach layer 3 to 3.5 microns.

Normalized Layer Elemental Composition, Ratioed to Si (atom basis)

	<u>Si</u>	<u>Mg</u>	<u>Al</u>	<u>Ca</u>	<u>Mn</u>	<u>Fe</u>	<u>Ni</u>	<u>U</u>	<u>Si/Total (%)</u>
Case 1	1.0	0.03	0.22	0.06	0.06	0.27	0.05	0.02	58.5
Case 2	1.0	0.07	0.28	0.10	0.10	0.44	0.09	0.02	47.6

bonding of the glass, making it more susceptible to leaching of the Si and hence about a factor of three more rapidly leached under the low SA/V conditions of the MCC-1 test.

The static test data demonstrate the effects of solution cation content and surface preparation on the chemical nature of the alteration layers; however, by far the dominant environmental variable in laboratory testing is the water flow rate. Even in ground water, where Si is present, high flow rates will maintain the alteration region in an unsaturated condition and promote continued, near-first-order dissolution of the glass (Chapter 1). In such cases the alteration zone becomes quite thick and exhibits distinct elemental distributions. The 30-micron-thick DWRG alteration zone shown in Figure 2.4 was produced using deionized water replacement to simulate high water flow. Elemental depth profiles of this sample are shown in Figure 2.17. These EDXS profiles demonstrate the high degree of Si depletion and the migration of elements within the layers. Mg, Mn, and Ni migrate to and appear to precipitate at the solution interface, while Fe builds up at the glass-alteration-layer interface. The profiles also show the well-defined interface that exists between the alteration zone and the bulk glass.

The layers formed in the high flow situation penetrate into the bulk as a moving front, with the rate approximately defined by boron release. The physical and chemical boundary between the alteration zone and the bulk glass is quite sharp, with alkali and boron depletion extending less than the resolution of SEM/EDXS (0.5 to 2 microns into the bulk). For the structural elements Si, Al, Fe, etc., this boundary is even more abrupt and can be seen by XPS. The XPS technique observes only the top 30 to 50 angstroms of a surface and is sensitive to chemical state changes. Figure 2.18 shows Fe 2p $3/2$ XPS spectra taken

from the glass beneath the separated alteration layers and from the top and bottom of the altered material. The chemical shift in the Fe spectra moves toward higher binding energies in the leached layer, indicating that the Fe is in a more oxidized bonding environment than in the bulk glass, and that the Fe is actually more oxidized at the outer surface of the alteration zone than at the bottom of the layer toward the glass interface. The XPS shows that the bonding changes within a 100-angstrom region between the glass and altered layer. This movement toward higher overall valence in the alteration layers was confirmed by electron paramagnetic resonance measurement (EPR). The EPR studies showed the Fe in the alteration layers to be dominantly +3, while the Fe in the glass is a mixture of +2 and +3.

Uranium is another multivalent element which shows oxidation in the alteration layer. The chemical shift and peak splitting of the U 4f electron levels (Allen et al. 1982) show the bulk U to be in a bonding configuration similar to UO_2 (Figure 2.19). Uranium found as crystalline uranyl on leached samples, however, is +6 valent.

The elemental migration observed in the alteration layers suggests that surface and interfacial charging play a significant role in the alteration process. Zeta potential measurements have shown that the waste glass surface has a negative potential, which could attract species with positive potentials such as $Fe(OH)_3$ and complexed uranium.^(a) Further study will be required to fully describe the role of Zeta potential and double layer charging in the alteration layer formation.

(a) Jantzen, C. M. 1984. "Electrochemical Stabilization of Waste Glass Surfaces in Aqueous Solution." To be published in Materials Research Letters.

FIGURE 2.17. EDXS Depth Profiles of the IAEA Leach-Tested Sample Shown in Figure 2.4

FIGURE 2.18. XPS Spectra of the Fe 2p Electron Levels in the Bulk DWRG and in the Alteration Layers. The spectra show the Fe to be more oxidized in the leached layers.

FIGURE 2.19. XPS Spectra of the U 4f Electron Levels in the DWRG and UO_2 . The comparison shows the DWRG to have U in the $UO_{2.x}$ chemical state.

In MCC-1 testing the low SA/V ratio requires that significant leaching of the glass occur before a steady state is reached. In this case polished and fractured samples of the DWRG typically develop layers from 1 to 3 microns thick in the time period (28 to 400 days) of the ongoing tests. These layers exhibit a much less dramatic distribution of the alteration layer elements, but do show the same trends found in the aggressively leached materials. In the leached sample of thermally fractured DWRG shown in Figure 2.2, the alteration zone had reached about 1 micron after 209 days. The elemental distributions from this sample in Table 2.4 show the same build-up of Fe at the layer-glass interface and surface enhancement of Mg and Ni observed with the IAEA leached sample described in Figure 2.17. The Mg is significantly more concentrated at the outer surface, indicating that it is being precipitated from solution.

To obtain more representative information on the chemical content of surface layers forming at the SA/V levels of a repository, monolithic samples of the DWRG were placed in the solutions of ongoing long-term water replacement tests with very low equivalent flow rates at Catholic University. XPS analysis of these samples showed clear indications of both dissolution and precipitation reactions. The spectrum in Figure 2.20 shows the elemental content of the top 30 to 50 Å of the approximately 300-Å-thick reaction zone formed in two weeks of exposure. Na is present on the surface at <50% of its original level, while Mn, Ni, and Mg have more than doubled their stoichiometric ratio to Si. Fe, and Ca show less dramatic changes. The increase of selected elements at the surface

demonstrates that significant dissolution has occurred, as does the absence of B, Li, and U. This indicates that Na and Mg are present as products of precipitation reactions, probably involving the precipitation of silicate phases.

A similar, but more dramatic, result was observed when polished monoliths of the TDS-131 glass were exposed to near steady-state solutions (pH 11.4) of the glass in deionized water at Catholic University. In this case, though leaching had progressed to a depth of about a micron into the glass, a marked enhancement of Cs was observed at the outer surface. The appearance of this soluble alkali (in analcime and montmorillonite-type clays) in the alteration layer emphasizes the role of precipitation reactions in establishing the chemical composition of the alteration layers under low-flow, high-SA/V leach conditions.

In simulated ground waters the chemistry of the alteration layers reflects the aqueous environment. In silicate water the surfaces were enriched in Si with respect to the rest of the alteration zone, presumably from surface silicate formation. However, in general the overall chemistry in the silicate water experiments was similar to that of the deionized water tests, though with an overall lower kinetic leach rate. Brine leaching is significantly different in that the pH of the system is lower than in either DI or silicate waters, being around 5.5, and the solution saturates very quickly with respect to mixed magnesium oxychlorides which form as precipitates on the glass surface.

TABLE 2.4. Elemental Distributions Determined by EDXS in a 1-Micron Alteration Layer Separated from a Thermally Fractured Sample of the DWRG (Figure 2.2). MCC-1 leach conditions; 209 days in static deionized water at 90°C. Uncertainty of determinations estimated at 10%.

Normalized Elemental Composition, Ratioed to Si (atom basis)								
	Si	Mg	Al	Ca	Mn	Fe	Ni	U
0.0-0.5 micron	1.0	0.14	0.39	0.10	0.13	0.46	0.10	0.03
0.5-1.0 micron	1.0	0.09	0.36	0.13	0.13	0.53	0.09	0.03
Bulk glass	1.0	0.02	0.16	0.04	0.04	0.15	0.03	0.01

FIGURE 2.20. XPS Spectra of a Clean DWRG Surface and a Sample That Has Been Exposed to a High-SA/V Leach Solution for 2 Weeks at 90°C. The short exposure under near steady-state conditions has produced both leaching and precipitation reactions.

These laboratory studies demonstrate that the alteration layers in waste glasses share the common features of soluble element depletion, species migration, and product precipitation. The extent to which these individual processes dominate is a function of the waste glass composition and the environmental variables. In all cases the alteration regions formed under conditions which led to lower leach rates in the DWRG (low flow, high SA/V, silicate water) exhibited significantly higher Si levels than those formed under conditions which produced higher leaching rates.

2.3. REACTION PRODUCTS IN STATIC AND LOW FLOW LEACHING

The waste glass-water interactions lead to the formation of several types of solid reaction products, which participate in establishing the steady-state solution concentrations of the waste elements. The rapid leaching of B, Li, and alkali from the glass leaves reactive sites at the glass surface where highly insoluble Mg and Ca precipitates can form in the very early stages of the dissolution process. As the glass dissolution continues, Fe and Si in the solution form colloids which can adsorb large charged cations released from the glass (Zr, U, actinides, rare earths, etc.). These complexes can agglomerate and produce flocculent amorphous precipitates. With further dissolution, saturation with respect to stable phases of the major elements (Si, Fe, and Al) occurs and hydrated precipitates, both amorphous and crystalline, form with consistent stoichiometry. The nature and abundance of the solid products are sensitive to all the reaction parameters, and as the reaction conditions change (pH rise, Eh drop, etc.) so may the identity of the products. This is especially apparent in the interactional tests with Fe metal present.

In most of the laboratory leach tests solid products can be observed on dehydrated samples by SEM/EDXS or XPS/SAM. However, only in long-term, high-SA/V experiments has sufficient material been collected to establish crystalline phase identities by XRD. Acceleration of the dissolution-crystallization process through the use of hydrothermal conditions has been pursued at the Rockwell International Science Center and Pennsylvania State University with some success. Results indicate a continuity in the back reaction pathways and product identities to temperatures as high as 250°C. The combination of the long-term tests at 90°C and the high-temperature studies does give a basic description of the types of phases that will play a role in establishing the ultimate solution concentrations of the glass ele-

ments, though the detailed solubilities and thermodynamic properties of many of the reaction products have yet to be determined in the laboratory.

2.3.1 Precipitates From the DWRG and TDS-131 Glass

The DWRG and TDS-131 glass, though similar in composition, have significantly different leaching properties in aqueous systems. As described in Chapter 1, the cation-anion balance in the TDS-131 glass results in continuing alkali release, which causes a pH excursion when the material is leached at high SA/V ratios. This glass in high-SA/V deionized water tests drives pH levels as high as 12.4. Under these alkaline conditions the glass dissolution can proceed to completion with the resulting products being present in abundance for characterization. The DWRG glass in comparison is more leach resistant and under high-SA/V conditions reaches solution pH levels of 10.3-10.7 after a year of testing. Consequently DWRG reaction products are much less abundant and more difficult to identify. The phases observed in the TDS-131 dissolution do, however, provide an indication of what types of products would be expected in longer time scales with the more stable borosilicate glasses. Table 2.5 lists the solid phases observed in long-term static and low flow simulation tests of the two glasses.

Figure 2.21 shows a fractured granule of the DWRG after 6 months of static deionized water leaching at an SA/V of approximately $1.2 \times 10^3 \text{ m}^{-1}$. Nodular precipitates are clearly visible as are deposits of amorphous flocculent material. Higher magnification SEM micrographs clearly show some of the nodular material to be well formed crystals whose XRD and EDXS spectra are consistent with a Cs-containing analcime, Figure 2.22 (ICDD 1983c). These analcime crystals were found in both the DWRG and TDS-131 deionized water leach tests with the only observable difference being that the TDS-131 tests produced a more Cs-rich stoichiometry. In the DWRG system the alkali had a Cs to Na ratio of about 0.01; comparable crystals in the TDS-131 system had a Cs/Na ratio of about 0.1. This Cs increase can be attributed to the higher pH and corresponding higher Cs solution concentration in the TDS-131 system.

Analcime is a natural mineral belonging to the zeolite family and is the sodium analogue of pollucite ($\text{CsAlSi}_2\text{O}_6$). The mineral is found in nature as a hydrothermal decomposition product from rhyolitic material and has been found with significant Cs content in

TABLE 2.5. Solid Reaction Products Observed in Dissolution Testing of the DWRG and TDS-131 Glass at 90°C
(Gnd = ground water, DI = deionized water)

Phase "Type"	Nominal Stoichiometry	Conditions
Mg silicate	Mg ₂ Si (sepiolite) ,Mg ₂ Si ₃ O ₆ (OH) ₄ ?)	DWRG & TDS-131 in DI & Gnd
Calcium sulfate	CaSO ₄	DWRG & TDS-131 in DI & Gnd
Analtime	NaAlSi ₂ O ₆ ·H ₂ O	DWRG & TDS-131 in DI
Weeksite	Na ₂ (UO ₂) ₂ (Si ₂ O ₅) ₃ ·4H ₂ O	DWRG & TDS-131, DI & Gnd
Tobermorite	Ca ₅ (OH) ₂ Si ₆ O ₁₆ ·8H ₂ O	DWRG & TDS-131, DI & Gnd
Montmorillonite type clays:		
	Na _n (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·xH ₂ O	TDS-131 in DI Water
Hydrated Al	Al(OH) _x (gibbsite, Al(OH) ₃ ?)	TDS-131 in DI water
alpha-Fe ₂ O ₃		DWRG + RCM in DI water
Discrete silicate phases observed in DWRG + silicate water tests:		
La, Al, silicate	(La, Al, Si, and Fe)	pH 10.6 at 20°C
Fe silicate	Fe and Si	pH 9.9 at 20°C
Ca silicate	Ca and Si	pH 9.6 at 20°C
Hydrated silica	Si and trace elements	pH 9.6 at 20°C
Ni silicate	Ni and Si	pH 9.6 at 20°C
Amorphous material	Variable (Si, Fe, Ni, Al, U, etc.)	All systems.
Brine testing produces mixed magnesium oxychlorides:		
	Mg ₂ (OH) ₃ (Cl) 4H ₂ O-Mg ₁₀ (OH) ₁₈ Cl ₂ ·5H ₂ O

FIGURE 2.21. SEM Micrograph of the Alteration Products Formed on a Sample of the DWRG After 6 Months of Static Leaching at 90°C in Deionized Water at a High SA/V.

such locations as Yellowstone (Keith, Thompson, and Mays 1983). Analtime is a commonly found product in the dissolution of silica-containing nuclear waste forms and has been reported by other investigators (Bates, Steindler, and McDaniel 1984).

The fibrous crystallites clinging to the analtime crystals in Figure 2.23 formed in clumps in the TDS-131 system and had a fairly complex XRD pattern. EDXS investigation showed that the clumped regions where the fibrous crystals joined were rich in Na, Si, and U, while the fibers themselves were primarily Ca, Si, and some Na. EDXS analysis (Figure 2.23) of the crystallites showed the clumped region to have the approximate stoichiometry, NaUSi₂₋₃O_x. This combined with the XRD pattern point to a weeksite-type phase prototypically Na₂(UO₂)₂(Si₂O₅)₃·4H₂O (ICDD 1983b). The fibrous crystallites have an appearance and stoichiometry (Figure 2.24) similar to a cementitious phase tobermorite, Ca₅(OH)₂Si₆O₁₆·8H₂O (ICDD 1983d), previously reported in the leaching of borosilicate glasses by Bates and Steindler (1983). The XRD pattern identification of this phase is not conclusive, however, and the crystals may be another calcium silicate.

FIGURE 2.22. SEM Micrographs and EDXS Spectrum of Analcime Formed in the 90°C Deionized Water Leaching of the DWRG at High SA/V. A similar analcime type formed in TDS-131 glass leaching has a factor of 10 higher Cs content.

FIGURE 2.23. SEM Micrograph and EDXS Spectrum of a Weeksite-Type $[\text{Na}_2(\text{UO}_2)(\text{Si}_2\text{O}_5)_3 \cdot \text{H}_2\text{O}]$ Uranium-Containing Crystalline Phase Formed in Both Silicate and Deionized Water Leaching of the DWRG and TDS-131.

FIGURE 2.24. SEM Micrograph and EDXS Spectrum of a Tobermorite-Type Product $[\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 8\text{H}_2\text{O}]$ Formed in Leaching of the DWRG and TDS-131 Glasses at 90°C at High SA/V.

One of the most abundant products of the long-term leaching of the TDS-131 glass is a flocculent precipitate found floating in the solution and adhered to the glass forms. This precipitate has no XRD pattern but does have a consistent stoichiometry. If the metal cations in the phase are grouped, a rough stoichiometry of $(\text{Na,Cs})_{0.5}(\text{Al,Mn,Fe})\text{Mg}_2(\text{Si})_4$ is obtained. This is similar to a group of Mg, Al, Si clays of the montmorillonite or smectite types (Ford 1983). It is this phase which is responsible for the greatly enhanced Cs content in the TDS-131 glass surfaces observed by XPS section 2.2.

Further examination of the surfaces of monolithic glass samples suspended in near-steady-state solutions of TDS-131 in deionized water produced isolated pockets of precipitate whose EDXS spectra was dominated by Al. These precipitates, Figure 2.25, are identified as hydrated Al, possibly gibbsite, $\text{Al}(\text{OH})_3$. Similarly isolated nodules on the DWRG glass surface have been found to contain only Ca and S and have been identified as CaSO_4 .

All analyses of leached samples routinely show Mg to be enriched at the outer glass surface, even in the initial stages. This precipitate has not been clearly identified in the deionized water systems since it is only present in a very thin layer at the outer surface of the waste form. In studies of glass leaching in dilute MgCl_2 solution, Grambow and Strachan (1983) have found sepiolite, $\text{Mg}_2\text{Si}_2\text{O}_6(\text{OH})_4$, to be the primary Mg-bearing precipitate and have shown this phase to be thermodynamically favored through comparison with the PHREEQE geochemical code. This phase, or a similar magnesium silicate, is the most likely product to explain the Mg build-up at the water-solid interface.

The reaction products in silicate ground water would not be expected to be greatly different from those observed in the deionized water case, except for the introduction of a broader range of anions. The silicate waters do, however, slow the laboratory reaction rates and limit the amount of reaction products produced. The TDS-131 glass, even in the ground water, still exhibits high alkali release and shows a rising pH which eventually produces conditions very similar to the deionized water leaching situation. The DWRG glass is more stable in the reference Grande-Ronde-type silicate water (Jones 1982) under static or low flow conditions with Mg, Si, and Ca build-up on the glass surface being the only short-term evidence of precipitate formation. In longer term (1 and 2 year) tests with powdered samples, crystal-

FIGURE 2.25. SEM Micrograph and EDXS Spectrum of a Hydrated Aluminum Containing Product Formed in Near-Steady-State Deionized Water Leaching of the DWRG at 90°C and High SA/V (as in Figure 2.20).

line products have been observed. In these tests the final pH values observed were dependent upon the SA/V ratio and are listed in Table 2.5. The weeksite-type uranium host phase was found as discrete crystallites floating in solution, and small pockets of La-rich precipitates were also found on the glass surface. The La, present as impurities in the DWRG, was only observed in these discrete precipitates; none was found in the surface layers. Other discrete deposits, rich in individual elements, were found in the DWRG-silicate water system, including a hydrated pure silica phase (Figure 2.26), a Ni silicate, a Ca silicate, and an Fe silicate. These results, combined with higher temperature hydrothermal data, support the phases listed in Table 2.5 as being characteristic products in the glass-ground water systems in the absence of canister metal.

FIGURE 2.26. SEM Micrograph and EDXS Spectrum of a Hydrated Silica Precipitate Observed in Silicate Water Leaching of the DWRG at 90°C and an SA/V of 360 m⁻¹

Brine solutions, with their high ionic content, behave markedly differently from the more dilute ground waters. The waste glass surface acts as a preferred location for the precipitation of Mg-containing species in these systems, with product build-up being significant after only 28 days of MMC-1 type static testing at 90°C. The surface precipitates are highly structured as can be seen in Figure 2.27, and tend to prefer roughened or scratched regions. Strips of gold placed in the containers with the glass show no such precipitation.

EDXS and XPS analyses of the products showed them to contain Mg, Cl, Al, and perhaps some Si, while the XRD pattern has only one strong peak. This makes definite identification difficult; however, the stoichiometry and Bragg reflections (ICDD 1983a) are consistent with a mixed magnesium oxychloride of the type $Mg_2(OH)_3(Cl) \cdot 4H_2O - Mg_{10}(OH)_{18}Cl_2 \cdot 5H_2O$, which has also been observed to be formed in the brine leaching of alumina-based polyphase ceramic nuclear waste forms (Jantzen et al. 1982).

The product identification results on the water-glass systems studied are supported by

previous work on MCC 76-68 glass in which hydrothermal leaching tests were run with glass, ground water, and basalt. These studies (Apted and Myers 1982; Myers, Apted, and Mazer 1983) were conducted under the Basalt Waste Isolation Program (BWIP) to determine the reaction products and ultimate elemental solubilities in interactive testing of waste glass and basalt repository materials. The BWIP hydrothermal studies found the dissolution products of the waste glass to include alteration products very similar to those formed in the DWRG tests. These included smectite clays, uranium silicates, hydrated silica, $Ca(OH)_2$, feldspars, and analcime/pollucite. These product types appear to be ubiquitous in waste glass-silica water systems and form a basis for the mineral types to be considered in solubility models.

2.3.2 DWRG + Canister Material + Deionized Water

The reactions of canister material with the DWRG were the most aggressive observed in static testing. Figure 2.10 shows the extent of the surface corrosion that occurs with the canister metal when it is exposed to the DWRG in air-saturated deionized water.

FIGURE 2.27. SEM Micrograph, EDXS Spectrum, and XRD Pattern of the Mixed Magnesium Oxychloride $[\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O} - \text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot \text{H}_2\text{O}]$ Preferentially Formed on the Surface of the DWRG in MCC-1 Static Leaching in Brine at 90°C for 28 Days

Figures 2.8 and 2.9 show several micrographs of the alteration layers formed in a 143 day MCC-1 type interactional test with the RCM material. The layers have a high degree of precipitate deposition and show an increased level of pitting of the bulk glass as described in section 2.1. Well formed star-like crystals were formed on the alteration layer, which have XRD and EDXS spectra similar to $\alpha\text{-Fe}_2\text{O}_3$ (meghemite or magnetite). The Fe-Si reactions occurring in this system accelerate the leaching process, but the solution concentrations of the waste elements are significantly lower than in control experiments with only the glass present. This is due to the high concentration of colloids

and flocculent precipitates in the system which scavenge the majority of the leached elements including the actinides (McVay and Buckwalter 1983; Chapter 4). These precipitates are mostly amorphous, but are expected to be iron silicates and hydroxides as predicted by the stability fields of mineral phases in the Fe-Si water system (Jantzen 1984a).

The performance of the interactive system is significantly different if deoxygenated water or glass-saturated ground waters are used in the leaching tests. Highly polished samples of the RCM introduced into a high-SA/V silicate water-DWRG leach test (pH >11) showed

only minor corrosion after 3 months exposure (though the glass was significantly leached), and tests at low Eh (-3 mV) carried out at the Savannah River Laboratory show only very slow reaction of the glass with the canister metal (Jantzen 1984a; Jantzen 1984b).

The interactional effects of the canister metal, glass, and ground water seen in these tests are highly dependent upon the solution oxygen content and other parameters. The interactive system does, however, quickly reach saturation with respect to solid products (colloids, complexes, and precipitates) which significantly reduce solution concentration levels for the waste elements below those found in glass-water control tests (Chapter 4). The mobility and absorption properties of the colloidal and precipitated complexes in ground water environments are currently not defined.

2.3.3 Saturation Products in Hydrothermal Leaching

The alteration of the glass surface under hydrothermal conditions is more rapid than at 90°C, but the results are a continuation of phenomena observed at 90°C. An altered layer develops on the glass, which readily cracks and separates from the bulk when dried. It also develops a fine scale network on the surface which is presumed to be a smectite phase as outlined previously. Crystalline phases are conspicuous alteration products in the hydrothermal experiments at elevated temperatures (particularly above 160°C, but seen at 138°C and as reported previously at 90°C); the absence and abundance of crystalline products and the fracturing of the thicker altered layers on the glass are presented in the sketches in Figure 2.28, where each sketch is positioned at the location of the corresponding experiment (see Figure 1.28, Chapter 1). This figure also illustrates how the early reaction enhances scratches in the original polished surface and how the scratches become subdued as the altered layer becomes thicker. Though not illustrated, there are examples of crystal aggregates arranged in lines on the glass surface, presumably along the traces of scratches. The first appearance of crystalline reaction products is in less than 24 hours at 250°C and in about 1800 hours (75 days) at 138°C for experiments with room temperature SA/V ratios of 2300 m⁻¹. Extending the line in Figure 1.28 to 90°C leads to the prediction of the appearance of crystalline phases by 4×10^4 hours (4-1/2 years), or for a product of surface area and time divided by solution volume of 9×10^7 hr m⁻¹, which is in good agreement with the observation (Figure 2.21)

of crystals in a run with a value of 5×10^8 hr m⁻¹. The crystalline phases identified in the hydrothermal experiments are summarized in Table 2.6. Smectite was not listed, although the smectite-like texture shown in Figures 2.1 and 2.34 are ubiquitous. The phases present at 90°C are also present at the higher temperatures, along with several others. Examples of each phase and typical EDXS traces are presented in Figures 2.29 through 2.33.

Analcline always contains appreciable cesium and shows good crystal morphology, either simple or complex (Figure 2.29). Analcline crystals were hand-picked from run 20-C, dissolved in acid and analyzed (DCP/AES); boron is present in significant quantities, as a partial replacement for aluminum. Searlesite, Na³SiO₂O₆·H₂O, is well known from low-temperature assemblages in boron-rich environments (Milton and Eugster 1959). In experiments which plot in the upper right corner of Figure 2.28, the analcline is abundant enough to form a pavement covering the glass (although this does not seem to affect the dissolution rate of the glass, see Chapter 1).

Weeksite appears in two distinct morphologies, crisp blades with blunt terminations or as thin, tapering crystals (Figure 2.30). There is no apparent difference in the chemistry of the two morphologies, although the first form occurs in the runs at higher temperatures and longer durations while the latter occurs as the first weeksite to appear. There are at least four distinct morphologies for the calcium silicates, all with approximately the same stoichiometry (Ca:Si about 1:2). The crystals and the spheres of calcium silicate in Figure 2.31 are from the same run. It is felt that they are the same phase, the spheres having nucleated earlier than the smaller separate crystals. This particular morphology consistently contains appreciable manganese and little Fe. A small amount of iron could be masked by the lesser manganese peak in the EDXS spectrum, but the ratio is appropriate to only manganese being present. The calcium silicate in Figure 2.32 consistently contains minor amounts of strontium and no detectable manganese (any strontium in the phase of Figure 2.31 is at or near the detection limit for the conditions employed).

Three more morphologies of calcium silicates are presented in Figure 2.33. The calcium-to-silicon ratios for these three phases are the same as for the preceding two phases, approximately 1:2, although there are no other elements consistently associated with them.

FIGURE 2.28. Plot of the Experimental Runs and the Reaction Results as Sketches of the Surface of the Glass Samples, Approximately as Viewed at 50X. In the lower portion of the figure, no crystalline phases were observed; scratches were enhanced by the reaction. In the upper portion of the figure, crystalline reaction products are common and their abundance and morphology are indicated.

TABLE 2.6. Crystalline Products Identified in Reaction of Glass and Water Under Hydrothermal Conditions

Run No.	Temp., °C	Time, hr	H ₂ O, g	Crystalline Phases Present
23 E	138	1800	0.1	calcium silicate
20 D	138	1800	0.3	calcium silicate
4 B	164	308	0.1	analcime, calcium silicate
9 D	166	950	0.1	calcium silicate
5 A	170	477	0.1	analcime, calcium silicate
21 B	175	360	0.1	analcime, calcium silicate
23 D	175	360	0.3	calcium silicate
20 B	175	360	1.0	analcime
24 E	174	1800	0.1	analcime, weeksite, calcium silicate
24 D	174	1800	0.3	analcime, calcium silicate
24 A	173	1800	1.0	analcime, calcium silicate
3 C	201	158	0.1	analcime, weeksite, calcium silicate, silica ^(a)
21 E	220	71	0.1	analcime, calcium silicate
23 F	220	71	0.3	calcium silicate
22 B	220	71	1.0	calcium silicate(?)
21 D	225	361	0.1	analcime, weeksite, calcium silicate
23 B	225	361	0.3	analcime, weeksite, calcium silicate
22 C	225	361	1.0	analcime, calcium silicate, weeksite(?)
20 F	230	1800	0.1	analcime, weeksite, calcium silicate, silica ^(a)
20 E	230	1800	0.3	analcime, weeksite, calcium silicate, silica ^(a)
20 C	230	1800	1.0	analcime, weeksite, calcium silicate, silica ^(a)
4 C	250	24	0.1	analcime, weeksite, 2 calcium silicates
3 D	247	102	0.1	analcime, weeksite, 3 calcium silicates

(a) Silica is used because only silicon could be identified by EDXS.

FIGURE 2.29. EDXS Trace and SEM Micrographs of Analcime Crystals. Upper right, analcime crystals with calcium silicate spheres, run 3-C (201°C, 1800 hr). Scale bars 50 microns.

FIGURE 2.30. EDXS Trace and SEM Micrographs of Weeksite Clusters. Left, tapered weeksite crystals over an analcime crystal, calcium silicate sphere (see Figure 2.34) to top right, run 3-C (201°C, 158 hr). Right, (run 20-F, 230°C, 1800 hr) bluntly terminated blades of weeksite; in the background are analcime, calcium silicate (Figure 2.31) and two forms of silica. (See Figure 2.34 right top and bottom). Scale bars 100 microns.

FIGURE 2.31. EDXS Trace and SEM Micrographs of Calcium Silicate Crystals from run 20-F (230°C, 1800 hr). Additional phase in right-hand panel is silica. Scale bars 25 microns.

FIGURE 2.32. EDXS Trace and SEM Micrographs of Fibrous Calcium Silicate Phase (run 21-D, 225°C, 361 hr). The shorter, brighter, feathery phase is weeksite. The disks are analclime crystals which were trapped between the glass slice and gold capsule when they grew. Scale bars 50 microns.

(A)

(B)

FIGURE 2.33. SEM Micrographs of Crystalline Calcium Silicates. The EDXS trace would be the same as Figure 2.32 except for the lack of Sr. (A), run 21-D (225°C, 361 hr). In (B) there are two morphologies present which give the same EDXS trace (run 3-D, 247°C, 102 hr).

The dominant phase in Figure 2.33b is similar to that identified as truscottite (Langton 1980). Neokite and okenite are two rare calcium silicate minerals with silicon-to-calcium ratios of 2:1. Truscottite is slightly more common and has a ratio of 12:7 (Fleischer 1983).

Tobermorite, several related phases, and gyrolite are the only other phases with a ratio of greater than 1:1. Tobermorite is common in cements with high silica-to-lime ratios and has a fibrous habit such as in Figure 2.32, although this is a common habit for calcium silicate phases.

The phases in Figure 2.34 all present the same EDXS pattern with only silicon present in significant amounts. This creates difficulties since the work of Liou (1971) predicts that analcime should not be stable with a silica phase above 200°C at 30 MPa, which is in agreement with our previous work (Freeborn et al. 1983). The stout prisms, which have a habit similar to that of quartz, were abundant enough in run 20-C that two dozen clusters of grains could be separated for analyses (DCP/AES), which showed that there is significant lithium and boron present in addition to the silicon. The array of laths resembles a sodium-lithium borosilicate phase reported by Savage (1981) from the hydrothermal alteration of a borosilicate glass.

From the compositions of the crystalline phases, the solution analyses, and the composition of the residual altered glass, it is possible to determine the fate of each of the elements in DRWG. These are summarized in Table 2.7.

2.3.4 Summary

The early formation of distinct precipitation layers in the alteration zone on the waste glass surface demonstrates the significance of both the dissolution and precipitation reactions in establishing the solution concentrations in laboratory leaching tests. The combination of the amorphous hydrated precipitates in the glass alteration layers, the crystalline precipitates, and colloidal material in the reaction system provides identifiable product species for all elements in the simulated waste glass except for perhaps B and Li. The crystalline precipitates are generally silicates whose stoichiometries are similar to natural analogues, though there are also a number of oxide and hydroxide phases formed. The phases observed in 90°C testing are consistent with those found in hydrothermal studies to 250°C, indicating that the precipitation reaction pathways do not dramatically alter over that temperature range.

FIGURE 2.34. EDXS Trace and SEM Micrographs of "Silica" Phases. Stout prisms (left): this morphology resembles that of quartz (SiO_2), although DCP/AES analysis shows the presence of Li and B in addition to Si, run 20-C (230°C, 1800 hr). Laths (bottom right): the individual crystals resemble those figured by Savage (1981), although the organization in the cluster is different (run 20-F, 230°C, 1800 hr). Ragged cluster (top right): sphere in background is calcium silicate (see Figure 2.33 A), run 21-D (225°C, 361 hr). Scale bars 25 microns.

TABLE 2.7. Disposition of Elements in DRWG Upon Reaction with Water

Al	analcline and altered layer of glass
B	primarily solution, also in analcline (partial replacement for Al) and in Li-B-Si crystalline phases
Ca	various crystalline calcium silicate phases
Cs	analcline (partial replacement for Na)
Fe	altered layer of glass
Li	primarily solution, also Li-B-Si crystalline phases
Mg	smectite
Mn	primarily altered layer of glass, also one of the crystalline calcium silicate phases
Na	solution, analcline and weeksite
Ni	altered layer of glass
Si	the crystalline phases, the altered layer of glass and solution
Sr	partial replacement for Ca in one of the crystalline calcium silicate phases
U	websites
Zr	altered layer of glass

The observed phases listed in Table 2.5 were not formed under equilibrium conditions and are not necessarily the thermodynamically favored products for the reaction system. The appearance of these steady-state and metastable products thus complicates a priori prediction of long term solution saturation concentrations from thermodynamic data (Paces 1978; Apted 1982, Chapter 7). The similarity of the reaction products to known mineral types, however, allows the data from observation of natural analogues and pure phase laboratory studies to be used in predicting long-range changes in the reaction products' chemistry and solubilities.

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CHAPTER 3
ENVIRONMENTAL INTERACTIONS

CHAPTER 3

Environmental Interactions

ASSIGNMENT: EVALUATE THE EFFECTS OF POTENTIAL REPOSITORY ENVIRONMENTS ON THE LEACHING OF WASTE GLASSES

SUMMARY: Waste glass will be encased in a 304L stainless steel canister, and ground water cannot contact the glass in the geologic repository environment until the stainless steel canister fails. Tests have shown that the residual stainless steel remaining after canister failure has no effect on glass leaching. But the immediate leaching environment in the repository will also contain additional metal, probably ductile iron, in the form of overpack or borehole casing, backfill consisting of fragmented repository rock and possibly a bentonite clay, plus ground water that is at least partially in equilibrium with this system.

Laboratory and field systems tests were carried out to evaluate the effects of these variables on the leaching mechanisms. In comparison to pure water, the rates of leaching for most elements are decreased in ground water and increased in the presence of bentonite and ductile iron (under oxic conditions). Ground water contains relatively large concentrations of silicon, which reduces the amount of silicon that can be extracted from the glass before saturation is reached and thus reduces the driving force for glass dissolution. Iron causes the formation of colloids while bentonite provides sorption sites. Both reduce the effective concentration of glass species in solution thereby increasing their extraction from the glasses.

Field tests have been conducted in a granite bore hole several hundred meters underground in the STRIPA mine in Sweden. The relative leach behavior of various waste glasses has been found to be the same in these field tests as in the laboratory tests. Sample configurations in the burial experiment provide high effective SA/V ratios which more closely approximate the physical condition of the repository than most laboratory tests. Under these conditions, waste glass leaching is low, again due to the same solubility effects observed in laboratory tests, and even the effect of bentonite seems to diminish after one year.

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CHAPTER 3.0

ENVIRONMENTAL INTERACTIONS

3.1 INTRODUCTION

The leaching performance of a waste glass will depend on the environment under which it is tested. In Chapters 1 and 2, glass leaching mechanisms and surface alterations were discussed in detail for an environment consisting of pure water under both static and flowing conditions. The environment to which the waste glass will be exposed will be more complicated and ultimately will be controlled by the system variables including geology, engineered waste package components, initial ground water chemistry, temperature, pressure, radiation field, water contact time and flow rate through the repository. It is the objective of this chapter to delineate important system variables (excluding the radiation field which is discussed in a separate chapter) and describe their effects on the leaching performance of waste glasses.

The Nuclear Regulatory Commission has endorsed a multibarrier approach for high-level waste management in regulation 10 CFR 60. Multibarriers are expected to provide long-term isolation of radionuclides through the appropriate combination of waste package design and geology. For this reason, current waste package design concepts and potential geological conditions are discussed in Sections 3.2 and 3.3, respectively. Release of radionuclides from the waste package will be used to provide a source term for modeling release rates from the repository. The primary focus of this chapter, however, is on determining the leaching performance of the glass itself and how this is affected by the presence of other waste package components and geologic conditions. Sorption and transport properties of the waste package components will be considered only with respect to their influence on glass leaching.

Laboratory and limited field tests were carried out using various combinations of reference materials in order to evaluate their effects on glass leaching. Although the field tests were not performed under actual repository conditions, they did provide a close simulation. The field test results

were consistent with those obtained in the laboratory for a wide range of waste-glass compositions. This finding is particularly important, since the burial and laboratory exposure conditions were not identical. The data suggests that the local environment produced by the combination of waste package components and physical system constraints control the leaching performance of the glass, and these can be reproduced in the laboratory.

3.2 WASTE PACKAGE

Nuclear waste glass-repository interactions potentially involve all components of the multibarrier waste storage system. The Engineered Waste Package (ONWI 1983) itself includes:

- a) borosilicate glass, which serves as the host matrix for the high level waste.
- b) a metal canister such as stainless steel, which is welded to form a hermetically sealed container after the glass is cast in it.
- c) a metallic overpack, of such materials as mild steel, ductile iron, pure titanium, or titanium alloy (Ti Code-12), and nickel alloys (Kircher, Moak and Clark 1983), which serves as an additional barrier for radionuclide containment.
- d) a sleeve, when required, which is used to assure clearance for the retrievable package to facilitate its removal during the retrieval period. It provides structural support against geologic pressure forces and may also serve as a barrier for radionuclide containment.
- e) backfill, the material contained between the other engineered waste package components and the host rock, which serves to facilitate heat transfer, load transfer and compatibility of the other engineered waste package components with the host rock. It may also serve as one of the barriers for radionuclide containment and

a sorptive medium for radionuclide release. Swelling clays such as bentonite, alone or in a mixture with quartz or other minerals, are being considered as backfill materials.

- f) a buffer, the material used to facilitate conditioning of the ground water, immobilization of radionuclides and compatibility of materials.
- g) a filler, which is any material used to fill space between other components of the engineered waste package and may or may not have other specified functions.

Waste package designs are still evolving and the components vary for different designs. Because of differing geologic and geochemical requirements for each type of site, not all designs use the same materials or components. For example, a backfill material may not be used in salt (Kircher and Bradley 1983). More complete descriptions of the waste package and the justification for design and materials selection are given by Kim (1984); Raines et al. (1981); Kircher, Moak and Clark (1983) and Kircher and Bradley (1983).

Interactions between the various components in the waste package with the host rock and ground waters will occur if the package is breached. These interactions will determine the long-term performance of the waste glass.

3.3 ENVIRONMENTAL CONDITIONS

It is not possible to define with exactitude the environmental conditions to which waste packages will be exposed in geologic repositories because repository design and siting explorations are not complete. However, sufficient instrumentation is available to bound the conditions quite well for the various candidate repositories. See, for example, Plodinec, Wicks and Bibler (1982) and Raines et al. (1981). These references demonstrate clearly that any repository ground water that contacts defense waste glass will be well below 100°C. Thus, most of the leaching mechanisms program testing was done at 70 or 90°C. It was also necessary to limit the number and types of materials that were used in the tests to evaluate environmental interactions. These materials, and the reasons for their selection, are described in the following subsections.

3.3.1 Ground Water Chemistry

The ground water chemistry can be defined in terms of water composition, pH and Eh. All

three variables are important because they affect glass solubility and hence its leaching performance. Typical ground water chemistries for several types of geologies are shown in Table 3.1. It can be seen that water composition varies within similar geologies and even within the same geologic formations. Additionally, pH and Eh are dependent on the type of rock to which the ground water is exposed.

Water composition is known to affect leaching. The presence of silica in ground water is beneficial since it reduces the driving force for glass matrix dissolution. On the other hand, carbonates can enhance the extraction of rare earths from the glass, and Mg-rich brines can enhance the dissolution of Cs and Sr from the glass.

In general, the pH of the basalt and granite ground waters is basic, while those in tuff and salt are nearly neutral. High pH conditions increase silica solubility compared to neutral pH values.

The ground waters in basalt are expected to be strongly anoxic while salt waters and tuff waters are expected to be mildly anoxic. Granitic waters appear to be slightly oxidizing. The low Eh in basalt ground water is most likely due to the dissolution of a redox active iron-rich phase under anoxic conditions (Jantzen 1983). Additionally, the presence of ductile iron can reduce the Eh and can drive the Eh to the lower limits of water stability under deoxygenated conditions (Jantzen 1983). Eh can have an important influence on waste glass leaching since many of the glass elements have more than one valence state (i.e., technetium and the actinides). The thermodynamics and kinetics of dissolution are dependent on the valence state of the element.

When the ground water reacts with various components of the waste package its chemistry may be significantly altered. Thus, the water contacting and reacting with the waste glass is expected to be different from that measured within the geologic formation. The presence of a redox active metallic material in the repository that can drive the Eh into the range of a stable silicate can produce synergistic effects that enhance the dissolution of both the glass and the metal. Two other important differences are the presence of colloids and sorption sites, both of which can act as chemical sinks and reduce the beneficial effects of saturation. These variables will be discussed in more detail in later sections.

TABLE 3.1. Groundwater Chemistries for Several Geologies (Analysis, ppm)^(a)

	Basalt					Granite			Salt	
	Grande Ronde		Interbed		Upper Wanapum	Stripa Mine		Nevada Test Site	WIPP Brine Inclusions ^(b)	WIPP Dissolved Core ^(c)
	A ^(a)	B	A ^(a)	B		A	B			
Na	363	250	107	83	34	125	73	51	42,000	115,000
K	3.43	1.9	11.2	11	11	0.4	1.0	4.9	30,000	15
Ca	2.76	1.3	2.0	4.7	17	59	24	14	600	900
Mg	0.032	0.04	0.4	1.8	8.8	0.5	0.5	2.1	35,000	10
F	33.4	37.0	1.3	2.2	0.7	3.7		2.2		
Cl	310	148.0	50	20	6.6	282	121	7.5	190,000	175,000
SO ₄	170	108.0	2.4	4.0	11.0	19	7.2	22	3,500	3,500
NO ₃				<0.5	0.5	0.28		5.6		
HCO ₃	55.1	43(25) ^(d)	215	217	177	12.8	35	120	700	10
CO ₃		34(21) ^(d)						0		
Si	35.6	56.6	14.0	32.3	26.6	18.7	5.5	28.5		
Al		0.11		0.30	0.086			0.03		
Fe		0.03		0.28	0.18	0.02	0.07	0.04	2	2
pH	9.75	10.1	8.5	8.7	8.1	8.95	9.3	7.1	6.5	6.5
Eh (Volts)		-0.52				+0.17		-0.1	>0	>0

(a) Wood and Salter 1980; Jones 1982; Smith et al. 1980; Gephart et al. 1979; ONWI 1981b; ONWI 1981c; ONWI 1981d; Raines et al. 1981; Fritz et al. 1979.

(b) Synthetic reference solution; pH value at room temperature.

(c) Also contains 1200 mg/L B (BO_3^{3-}) and 400 mg/L Br^-

(d) also contains 10 mg/L B (BO_3^{3-}) and 400 mg/L Br^-

(e) Values calculated from the pH and ionic balance given by Smith et al. (1980) are given in parentheses.

Since the potential range of repository environments is too large to evaluate, we selected several reference conditions that were used for the majority of the data reported in this document. These conditions, and the rationale for their selection, are discussed in the next section.

3.3.2 Reference Conditions

Four primary reference materials were used for the majority of the experiments conducted during this investigation (see Table 3.2). These were: 1) Defense waste reference glass (DWRG), 2) deionized water, 3) synthetic

TABLE 3.2. Reference Materials Used In This Investigation.

Constituent	Reference Synthetic Groundwater ^(a)	STRIPA Ground Water		MCC Reference Silicate Water	MCC Reference Brine
		Analysis 1 ^(b)	Analysis 2 ^(c)		
NA	358	51.5	55.1	30	54,600
K	3.43	0.2			
Ca	2.78	16.2	14.9		
Mg	0.032	0.25	0.25		29, 610
Si	35.57	5.2	6.2	7	
F	33.4				
Cl	312	56.0			163, 910
SO ₄	173	3.1			
HCO ₃ + CO ₃	55	84.4		130	
pH	9.75	9.1	8.3	7.5	6.5

(a) Jones 1982.

(b) Fritz, Barker and Gale 1980.

(c) Measured at University of Florida.

(d) Johnston and Daniel 1982.

ground water based on the formula given by Jones (1982), and 4) ductile iron.

When glass reacts with pure water the solution chemistry undergoes alteration until equilibrium is established in the system. Equilibrium, the rate at which it is approached, and the resulting glass surface alterations are dependent on the initial water chemistry. Since the waste glass itself is fairly complex in structure and composition, deionized water was used as a reference leachant because it provided the simplest environment in which to study the glass leaching mechanisms. The deionized water used at the University of Florida and most other participating laboratories was air-saturated with a pH = 5.68, while the deionized water used at Catholic University of America was saturated with nitrogen and had a pH = 7.0.

Since a major goal of this investigation was to evaluate glass leaching performance in realistic environments, a reference leachant other than deionized water was needed. One option was to use water extracted from the ground, but water chemistry is altered once it is removed from its natural environment. Additionally, fairly large quantities of water were required in the leaching experiments, especially those involving flow. Thus, water stability, availability and consistency were the major drawbacks to using

natural ground waters. Jones' synthetic ground water was selected as a reference leachant for several reasons. First, its composition is known and the method of preparation is straightforward, thus facilitating its use in all of the laboratories participating in this investigation. Secondly, its composition and pH are fairly representative of several hard rock geologies. In fact its composition closely matches that for ground water at a 1-km depth in the Grand Ronde Basalt formation (Wood and Salter 1980; Jones 1982). One problem was encountered with its use. Upon storage, the concentration of Mg decreased probably due to precipitation. The magnitude of this change appeared to be slight. The tests involving the synthetic ground water were carried out under ambient conditions without attempt to control solution Eh.

Ductile iron was selected as the reference material simulating the metallic overpack. Iron most likely will be the most reactive metal in the waste storage environment, and thus will have the major influence on glass leaching performance. This material was supplied to each of the participating laboratories by the Materials Characterization Center (see Appendix A).

Other materials listed in Table 3.2 were used as reference materials by the University of Florida for several laboratory and

field tests. These include Wyoming Na-bentonite,^(a) a potential overpack/backfill material, and water from the Stripa mine in Sweden (Fritz, Barker and Gale 1980).

3.4 EFFECT OF GROUND WATER CHEMISTRY ON GLASS LEACHING

For nearly all repositories it is probable that water will eventually come into contact with interfaces containing high-level waste (HLW). The effects of temperature, flow rate and contact time (flush time) on glass leaching are discussed in detail in Chapter 1 for pure water. Ground water chemistry and its effect on glass leaching performance is the main focus of this section. Since current concepts in waste package design and disposal indicate that water coming into contact with the waste form will be less than 100°C, discussion will be limited primarily to this same range (Kircher, Moak and Clark 1983).

There have been two general approaches for evaluating glass-ground water interactions. In one approach the glass is immersed in water with a fixed chemistry usually simulating ground water from one of the potential repository geologies. The other approach involves the addition of a second solid (rocks and/or waste package components) to the water along with the glass. Both types of tests may indicate differences in the leaching performance of the glass in comparison to that obtained in pure water. These differences are expected since the ground water, with and without rocks or waste package components, has a different pH, Eh and composition than pure water; each of these variables has been shown to influence glass leaching.

A comprehensive study was performed by Wicks, Robnett and Rankin (1982) in which they compared leaching behavior of a defense waste glass in deionized water, ground water and both waters containing rocks. Their analyses were based on the concentrations of species in solution and did not take into consideration the species adsorbed onto solids present in the leaching vessel. They found that the presence of salt (from Carlsbad and Avery Island), basalt, shale, granite and tuff all slightly decreased the concentrations of glass species in solution compared to those obtained when deionized water was used alone. Similar results were found with synthetic ground waters and with the same waters containing the various rocks.

(a) Volclay MX-80; from Christensen et al. 1984.

Actual ground waters yielded results comparable to the MCC reference waters and synthetic ground waters.

Clark and Maurer (1982) investigated the effects of several types of rocks including basalt and granite on the leaching of a borosilicate glass. With the possible exception of granite, the combination of glass and rocks in the same leaching vessel did not appear to have any significant effects in a 28-day test. Other leaching experiments using combinations of glass and rocks have been reported, but many are not directly relevant to the current study since they were performed under hydrothermal conditions.^(b)

Interpretation of data from the tests involving solids as well as glass is complicated for at least two reasons. First, the solution chemistry may or may not be significantly influenced by the dissolution kinetics of the second solid, making it difficult to sort out those changes due only to the glass. Secondly, the solid can provide sites onto which species leached from the glass may be adsorbed.^(c) The extent of sorption is strongly dependent on the element, its oxidation state and temperature (Brookins 1984). An apparent discrepancy would be obtained between leach rates measured from solution analyses and those measured from surface analyses with the former being lower. In fact, an increase in the leach rate measured from surface analyses may be accompanied by a decrease in the leach rate calculated from solution data due to sorption effects. As an example, bentonite (Hench, Werme and Lodding 1982) and other clays (van Iseghem, Timmermans and Batist 1982) increase the rate of glass leaching, while the presence of granite can either slightly increase or decrease the rate of leaching depending on SA/V.^(d) Wet clay attacks the glass faster than a clay/water mixture containing less clay (van Iseghem, Timmermans and Batist 1982). These effects are presumably due to

(b) Apted and Myers 1982; Apted 1982; Salter and Jacobs 1982; Apted 1981; Cotes 1984; Malow 1982; Scheetz et al. 1980.

(c) Hinkenbein and Hlava 1979; Barney 1979; Nowak 1980; Komarneni and Roy 1980; Gancarz et al. 1980; Erdal et al. 1980; Beall et al. 1980; Lynch and Dosch 1980; Vine et al. 1981; Sasaki et al. 1982; Allard et al. 1982; Salter and Jacobs 1982.

(d) L. L. Hench, A. R. Jurgensen, A. Lodding and L. Werme. "Effect of Uraninite on Nuclear Waste Glass Surface Behavior." To be published.

an ion exchange between the glass and sorption sites on the silicate surfaces that prevent leachant saturation of many glass species. Based on glass surface analyses alone, the presence of bentonite and other clays might be considered deleterious. However, bentonite and other clays, in addition to having the desirable backfill properties, are known to sorb many of the radionuclides (Nowak 1981; Erickson 1980) leached from the glass, thus reducing their release rates from the waste package.

Numerous studies in the absence of rocks have been conducted which permit a few generalizations about the effects of ground water composition on glass leaching. Static MCC-1 tests on TDS-131 glass in MCC silicate water have shown that the dissolution rate of Si is lower by about 40% than in deionized water (Plodinec, Wicks and Bibler 1982). A round robin leaching test involving PNL 76-68 glass also indicated that the leaching rates of B, Cs and Sr as well as Si were lower in MCC silicate water (Hench and Clark 1981). Pederson et al. (1983) have shown that the leach rate of Si, B and other soluble glass components exhibit an approximate inverse relationship to the amount of Si initially present in the leachant. These results are significant because they involved the use of both silicic acid and ground waters and are consistent with the findings of Wicks, Robnett and Rankin (1982) that leaching in the simpler MCC waters is comparable to the more complicated actual ground waters. Bradley et al. (1983) have compared the leaching of B and Cs from PNL 76-68 in simulated Hanford site basalt ground water, tuff ground water from Well J-13 at the Nevada Test Site, and deionized water. The extent of B and Cs leaching was less in the ground waters than in the deionized water, with basalt water producing the least leaching. Glass exposed to the deionized water exhibited the characteristic initial rapid release rate which decreased with time. There was little evidence of an initial enhancement of leach rate in basalt or tuff water. These results suggest that solution composition controls the leaching characteristics. The higher the initial concentration of element in the leachant, the slower its leach rate will be from the glass. An additional important conclusion from the study reported by Bradley et al. (1983) was that SA/V variations can be used for time compression in basalt and tuff waters as well as deionized water. This permits the use of high SA/V for predicting glass leaching behavior over time periods not possible in laboratory experiments. Whereas the leaching rate of most elements appear to be suppressed in

silicate waters, Plodinec, Wicks and Bibler (1982) and Stone (1982) found that the leaching rate of U was enhanced to the same level as Cs and Si.

An investigation by Chapman and Savage (1980) on the leaching behavior of United Kingdom glasses in granitic and deionized waters revealed very little difference during the first several hundred hours. It appears, however, that if their data are extrapolated to longer times, the leaching rate based on weighing would be less in ground water.

In one study, the leaching rate of the major glass constituents has been reported to be higher in MCC silicate water than in deionized water (Hermansson et al. 1983). The glasses used in this study were of the Swedish types ABS 39 and ABS 41. These same glasses were also found to be very sensitive to the presence of CO₂ in solution; the higher the CO₂ content, the greater the leach rate. The higher leach rates are thought to be related to the formation of insoluble rare earth carbonates that alter the surface layer of the glass and its leaching characteristics. Preparation of the MCC silicate water requires the use of carbonates which could be the reason for the increase in leach rates.

Brine solutions generally decrease the rates of elemental leaching (Hermansson et al. 1983; Wicks, Robnett and Rankin 1982; Malow 1982) with the exceptions of Sr (Strachen, Barnes and Turcotte 1981; Strachen 1982), Ce (Strachen, Barnes and Turcotte 1981), Cs (Strachen 1982) and Ca. In one case Stone (1982) has shown that the leaching rate of Cs is reduced in brine solution during the first 28 days of exposure. Strachen (1982) reported a similar result, but showed that the leaching rate was higher after 365 days in brine solution than in deionized water. The reason for the increase in Cs (and Sr) leaching observed in brine solution is related to surface layer formation. In deionized water (and also in silicate water), a zinc silicate layer is formed with time which can accommodate Cs and reduce its solution concentration. In contrast, the magnesium silicate layer that forms on PNL 76-68 in brine solution does not adsorb or concentrate Cs or Si within it. Tests in salt brines containing high magnesium concentrations indicate that the formation of an alteration phase containing Si, Fe, Mg among others, causes continued leaching of the glass after saturation should have otherwise substantially reduced dissolution (Pederson et al. 1983). Thus, the leaching rates of many of the major glass constituents (and U; Stone 1982) may be reduced in brine solution,

while the leach rates of elements not incorporated in the alteration layer may appear enhanced in comparison to deionized water. Shade, Pederson and McVay (1984) evaluated the effects of a synthetic brine on the leaching behavior of MCC 76-68, and their results are in agreement with earlier studies. Hydrolysis of the glass was generally lower in saturated brine than in deionized water due to the lower solubility of silica in brine. However, the dissolution rates of Cs, Sr and Zn were enhanced in brine solution compared to deionized water. SIMs analysis revealed that although the depths of Cs leaching were the same in both solutions, Cs was more thoroughly removed from the leached layer in brine. SIMs analysis also confirmed the presence of a Mg-rich layer on the glass surface exposed to brine.

Hermansson et al. (1983) found that brine solutions decreased the leach rates of most glass elements with the exception of Si (i.e., did not measure Cs) in comparison to deionized water. The removal of Sr from the glass was significantly increased in brine solution. The enhanced Sr leach rate in brine has been explained by Strachan (1982) as being due to a reduced pH, preventing precipitation. A solution containing pure NaCl (1000 ppm of Na) produced one of the most aggressive environments and it increased the leach rate of all elements measured. Apparently, an alteration layer is not formed in pure NaCl solution.

Results of a MCC 28-day round robin test on PNL 76-68 indicated that the leach rate of Cs was slightly lower [i.e., consistent with Stone (1982) and Strachan 1982)], while the leach rate of Sr was significantly higher (consistent with Strachan and Hermansson) in brine solution compared to deionized water (Johnston and Daniel 1982). The leach rate of Si was also significantly decreased in brine solution compared to deionized water.

Braithwaite (1980) obtained similar results for the leaching of Cs in brine solution at 250°C. Although the amount of Cs leached from the glass was found to be dependent on the SiO₂ concentration in solution and SA/V, in general brine solutions resulted in less Cs leaching over a 28-day period than did deionized water.

Very few studies have been conducted to evaluate the effects on glass leaching of ground water under flowing conditions. Bradley, Harvey and Tyrcotte (1979) investigated the release of ²³⁹Pu and ⁹⁹Tc from PNL 76-68 in both deionized water and salt brines at 22°C using an IAEA test. This test

requires that the leachant be changed at regularly scheduled intervals which simulates a continuously flowing condition. Under these conditions Pu leaching was less in the brine solution than in the deionized water, whereas the reverse trend was observed for Tc. Other elements investigated included ²⁴⁴Cm, ²³⁷Np, ²⁴³Am and ²³³U; the extent of leaching in brine was different for each element with Np being the most extensively leached. Plodinec, Wicks and Bibler (1982) studied the leaching of ¹³⁷Cs from an actual Savannah River Plant waste glass using a modified ISO test. This test also requires solution replenishment at scheduled intervals and approximates a flowing condition. There was no difference between the leaching of Cs after 1 year in deionized water and magnesium brine solution. Weed et al. (1980) compared the leach rates of ²³⁷Np and ²³⁹Pu in brine and distilled water as functions of temperature and flow rate. They used a single pass flow test similar to the one discussed in Chapter 1. They found that the leach rates increase with flow rate at 75°C but are approximately independent of it at room temperature in both distilled water and brine. They also found that under flow conditions there was very little difference in leach rate between the distilled water and brine.

A comparison of the leaching performance of DWRG in three different leachants under static conditions is shown in Figure 3.1. The concentrations of boron and lithium are used for the purpose of illustration because neither initially is present in the leachants. The concentrations of these elements increase with exposure time in all three solutions, but do not achieve saturation even after 28 days. Both the synthetic ground water and the Stripa water reduce the extent of boron and lithium removal from the glass when compared to deionized water. Furthermore, the total weight loss of the glass is greater in the deionized water when compared to the other two leachants.

The Stripa water provides the least aggressive environment although its silicon content is less than that in the synthetic water (see Table 3.2). One possible explanation for this behavior is the presence of higher concentrations of anions such as Cl⁻, F⁻, SO₄²⁻, and HCO₃⁻ in the latter leachant. These ions can potentially complex (Brookins 1984) with, or precipitate species (Hermansson et al. 1983) leached into solution from the glass. Hermansson et al. (1983) have shown that high concentrations of carbonate ions in solution result in accelerated attack on the ABS 39 glass. The major point to be made here,

FIGURE 3.1. Boron and Lithium Concentrations and Normalized Total Mass Loss Due to Leaching DWRG in Deionized Water, Synthetic Silicate Water and Stripa Water Under Static Conditions.

FIGURE 3.2. FTIRRS Analysis Before and After Leaching for 28 Days at 90°C in (a) STRIPA Ground Water with $SA/V = 0.1 \text{ cm}^{-1}$, (b) STRIPA Ground Water with $SA/V = 1.0 \text{ cm}^{-1}$, and (c) Deionized Water with $SA/V = 0.1 \text{ cm}^{-1}$. Hatched areas correspond to the range of values obtained with several samples.

however, is that ground waters reduce the extent of DWRG deterioration in comparison to deionized water under static condition.

Direct evidence of the beneficial effects of ground water is provided with surface analyses of the glass itself, shown in Figure 3.2. Reflection spectra of the glass surfaces, obtained with a fourier transform infrared spectrophotometer, are shown for the glasses exposed to the Stripa and deionized waters. The decrease in percent reflectance relative to the uncorroded glass is a measure of the extent of surface alteration due to leaching. Based on this interpretation, Stripa water results in less leaching than does deionized water when other conditions are equivalent. Figure 3.2 illustrates the effects of another important variable in glass leaching, namely, SA/V . The extent of leaching in ground water is reduced when the SA/V is increased.

The tests described above were all performed without any effort to control the atmosphere above the leachants. The presence of CO_2 is known to provide a weak pH buffer which can potentially affect test results. The extent of CO_2 dissolution in the leachant and its

buffering capacity are directly proportional to the partial pressure of CO_2 . In order to evaluate CO_2 effects on DWRG leaching, a modified MCC-1 static test was used. The atmosphere above the leachant was varied, however, as shown in Table 3.3. A pure CO_2 atmosphere provided the best buffering and the least weight loss. Within the range of experimental error there was no significant difference in weight loss between an ambient

TABLE 3.3. Effects of Atmosphere on DWRG Leaching. Test conditions were 90°C, 28 days, $SA/V = 0.1 \text{ cm}^{-1}$ and deionized water.

Atmosphere	pH	Normalized Total Mass Loss (g/m^2)	% RSD(a)
Ambient	8.57	4.06	10.33
Pure CO_2	6.02	1.74	53.3
Pure Nitrogen	7.22	4.22	13.9

(a) Relative Standard Deviation. See Section 3.9 Appendix for explanation.

environment and one consisting of pure nitrogen. All continuous flow test data reported in the chapter were obtained under ambient atmosphere conditions, while pulsed flow test data for deionized water were obtained in a pure nitrogen atmosphere.

The effects of silicate ground water on the static leaching behavior of DWRG are the same as those reported in the literature for other U.S. waste glasses. Initial leachant composition assumes a major role in glass leaching by controlling the extent of dissolution required to produce saturation. When silica is initially present in the leachant, its concentration gradient through the glass-

solution interface is reduced, which reduces its driving force for dissolution from the glass. This effect is illustrated schematically in Figure 3.3 where the concentration versus time curve is shown. The leach rate of silica from the glass can be represented by the slope of the curve. The greatest slope, and hence the largest leach rate, occurs when the concentration of silica in solution is equal to zero. In a static leach test the leach products accumulate in solution and eventually approach saturation. The leach rate of silica decreases as its solution concentration increases. When the solution becomes saturated with respect to silica, its leach rate, as measured by its

FIGURE 3.3. Schematic Illustrating the Relationship Between Concentration, Contact Time, Flow Rate and Leach Rate

change in solution concentration, will be zero. Based on this explanation, it can be seen from Figure 3.3 that the leach rate of silica in deionized water, where its initial concentration is zero (C_2), will be greater than the leach rate of the same element in a leachant with an initial concentration equal to C_2 or C_1 . Of course each element has a different saturation concentration, but since silica is the major structural component of the glass a reduction in its dissolution will result in concomitant reduction in dissolution of the other glass constituents.

Similar effects of ground water on DWRG leaching are found under conditions of flow. Figure 3.4 compares the pH and release of boron and lithium in deionized water with synthetic silicate water under static conditions and at flow rates of 0.1 mL/h and 1.0 mL/h, corresponding to contact times of 600 h and 60 h, respectively. Strontium data is presented for the lower flow rate. Many of the important features of such curves were discussed in Chapter 1. Under conditions of flow there is an initial increase in boron, lithium and strontium solution concentrations followed by a decrease until steady state is achieved, when their concentrations are independent of time. The time required to achieve steady state decreases as the flow rate is increased. Steady state concentrations are dependent on flow, however, and decrease as the flow rate increases for boron and lithium in both types of water. The trends in concentration versus time are nearly the same for deionized and silicate water. Steady state concentrations are lower for both elements in the silicate water. One other important observation can be made from Figure 3.4. The difference between the steady state boron concentration in the two leachants decreases as the flow rate is increased. At a flow rate of 0.1 mL/h the difference in concentrations is about 1 ppm, while at a flow rate of 1.0 mL/h the difference is about 0.1 ppm. The same behavior is observed for lithium (Figure 3.4b) and for sodium (not shown).

The effects of silicate water under flowing conditions can be explained by referring to Figure 3.3. Under static conditions the concentration will increase with time until saturation. When the solution flows at a sufficiently rapid rate saturation will be prevented and the concentrations of most elements in solution will be reduced. A constant value of concentration will be found for each element in the solution flowing out of the leaching vessel. This value is controlled by a combination of the element's leach rate from the glass and its rate of

removal (i.e., flow rate) from the leaching vessel. Steady state is achieved when these two rates are equal and there is no measurable change in the concentration of the egressing solution. If the flow rate produces a steady state concentration equal to C_2 for any element, its leach rate will be $(LR)_2$. Higher flow rates result in lower steady state concentrations and higher leach rates.

The steady state value is also dependent on the initial composition of the solution. If the leachant contains an initial concentration of an element, C_2 , before coming into contact with the glass the initial leach rate of that element from the glass will be $(LR)_2$. During the time that the solution remains in contact with the glass (i.e., inversely proportional to flow rate), the concentration of that element will increase from C_2 to its steady state value C_1 . Its steady state leach rate will be reduced from $(LR)_2$ to $(LR)_1$. The higher the flow rate, the less the contact time and the smaller the change from $(LR)_2$ to $(LR)_1$. In the limiting case of high flow rate, the steady state concentration will be C_2 and leach rate will be $(LR)_2$ for the leachant containing an initial concentration of C_2 . When the leachant is pure water, the limiting concentration under high flow conditions will approach zero. As the flow rate increases, the differences in steady state concentrations of the leachants should diminish but will never get closer than a value equal to C_2 .

The effects of silicate water on DWRG leaching was also evaluated under dynamic conditions using a pulsed flow test. Table 3.4 summarizes these results for many of the important elements in the glass. In general the concentration of glass elements in solution are less in the silicate water than in deionized water under equivalent test conditions and corrected for initial concentrations in the leachants.

The final pH achieved in solution was dependent on both the flow rate and leachant. In deionized water the pH increased from its air-saturated value of 5.68 to about 9 in the static test. The highest value obtained in deionized water at a flow rate of 0.1 mL/h was 7.5, and this decreased to a steady state value of about 7 to 7.2. Similarly, the solution pH rose to about 7 at a flow rate of 1.0 mL/h and then decreased only slightly over 28 days. In contrast, the pH of the synthetic water decreased slightly under static and flowing conditions. It should also be noted that although the solution pH of the synthetic water was in the range where

FIGURE 3.4a. Boron Concentrations Resulting from Leaching DWRG in Deionized Water and Silicate Water Under Flowing Conditions

FIGURE 3.4b. Lithium Concentrations Resulting from Leaching DWRG in Deionized Water and Silicate Water Under Flowing Conditions

FIGURE 3.4c. Strontium Concentrations Resulting from Leaching DWRG in Deionized Water and Silicate Water at a Flow Rate of 0.1 mL/h

FIGURE 3.4d. pH Versus Time for the Deionized Water and Silicate Water Water Exposed to DWRG

FIGURE 3.4e. Normalized Total Mass Loss (g/m^2) Versus Time for DI Water and Silicate Water With and Without Iron, and STRIPA Water Exposed to DWRG

silica dissolution usually increases, saturation effects prevented dissolution. The fact that saturation is more important than pH is clearly seen under flowing conditions, where the pH of the deionized water is much less than the synthetic water, yet the leach rates are much higher in the former.

3.5 EFFECTS OF IRON AND OTHER WASTE PACKAGE COMPONENTS

The waste package is expected to assume an important role in the final disposal and immobilization of the radionuclides. Various components are being included in the package to minimize contact of the waste glass with water during the thermal period, and to ensure that radionuclides do not escape should breachment occur. However, in selecting package materials to perform specific functions, their potential interactions with the waste glass that could affect leaching should also be considered. The data required to make the proper selections have only recently begun to appear in the literature. Based on current concepts, the waste package, in addition to borosilicate glass, may contain stainless steel, iron, titanium, and bentonite, among others. Thus, it is important to understand their interactions with ground water as well as any synergistic effects these interactions may produce with the waste glass.

The effects of various metals on waste glass leaching has been reported by Buchwalter and Pederson (1982), McVay and Buckwalter (1982)

and Shade, Pederson and McVay (1984). These investigators found that copper, tin and titanium had no effect on glass leaching, while lead and aluminum significantly reduced the leached rates. The beneficial effects of Al (in solution) have also been observed on other glasses (Iller 1973; Dilmore et al. 1979). The presence of aluminum, lead and stainless steel on the leaching behavior of both SRL 131 + TDS and PNL 76-68 under flowing conditions have been investigated by Barkatt et al. (1983b). Their results are in agreement with those presented above for aluminum and lead. Additionally, stainless steel specifically reduced the concentration of Ca and Sr in solution, whereas the leach rates of Li, Na, Cs, B and Si were not affected. These results are in agreement with those from tests conducted in granite boreholes where the presence of stainless steel did not appear to appreciably alter the leach rate of several types of glass (Werme, Hench and Lodding 1982; Wicks and Ross 1984a; 1984b).

A difference in leaching behavior has been reported on small stainless steel canisters containing glass for the glass near the interface compared to the glass far away from the interface (Clark, Urwongse and Maurer 1982). This difference was not due specifically to the presence of stainless steel, but more likely to either the differences in glass composition near the interface or stresses in this region.

The most significant effect on nuclear waste glass leaching due to the presence of a metal was first observed by McVay and Buckwalter (1982), who found a synergistic effect between ductile iron, various ground waters, and PNL 76-68 glass under oxic conditions, (i.e., normal atmosphere). The leaching rates of both the glass and iron were found to be enhanced when placed in the same solution. Figure 3.5 illustrates these results. In the absence of iron, it can be seen that tuff and basalt waters reduce the extent of leaching compared to deionized water. However, with iron the beneficial decreases in leach rates in ground water are eliminated, and in fact the leach rates in all three solutions are significantly above that obtained with deionized water alone. The reason for enhanced glass leaching in the presence of iron, as explained by McVay and Buckwalter, is due to the formation of an iron silicate precipitate, part of which is colloidal in nature. The precipitate effectively reduces the concentrations of elements in solutions thereby increasing their leach rates. This is illustrated conceptually in Figure 3.3. Recall from previous discussions that the leach rate

TABLE 3.4. Effects of Ground Water on DWRG Leaching Under Dynamic Testing Conditions; Monolithic Samples, 90°C

SA/V (m ⁻¹)	Tr (days)	Leachant	pH	Leachate Concentration (mg/l)								
				Si	B	Li	Cs	Sr	Ca	Al	Fe	U
0.0(a)		GW	9.71	34.7	0.01	0.00	0.00	0.00	4.88	0.05	0.00	0.00
10.7	4	DIW	9.04	3.67	0.40	0.38	0.136	0.031	0.12	0.36	0.054	0.048
10.5	4	GW	9.58	35.4	0.14	0.14	0.011	0.044	4.97	0.25	0.001	0.059
10.7	28	DIW	9.05	12.1	1.28	1.26	0.25	0.106	0.46	0.79	0.06	0.21
10.5	28	GW	9.40	39.9	0.32	0.34	0.07	0.093	4.59	0.44	0.02	0.28
266	28	DIW	10.00	50.1	6.90	6.22	0.78	0.072	0.27	4.05	0.39	0.88
224	28	GW	9.55	50.2	1.84	1.63	0.40	0.289	4.05	1.12	0.02	0.65

(a) Pure synthetic groundwater; Al and B present as impurities; additionally contains 357 mg/l Na, 6.08 mg/l K, 0.014 mg/l Mg, 309 mg/l Cl⁻, 38.6 mg/l F⁻, 190 mg/l SO₄²⁻ and 55 mg/l of (HCO₃⁻ + CO₃²⁻); prepared according to Jones (1982).

FIGURE 3.5. Illustration of Two Effects on Leaching Characteristics of PNL 76-68 Glass, i.e., Effect of Groundwater Without Iron Present and Effect of Having Iron Present During Leaching

depends on solution concentration; the higher the concentration the lower the leach rate. The presence of iron shifts the leach rates towards the left (i.e., lower

concentrations and higher leach rates) in Figure 3.3. Although ground water shifts the leach rates to lower values, the magnitude of this shift is small, and thus the net shift is to the left when both iron and ground water are present. Similar results were found by Shade, Pederson and McVay (1984) in a brine solution containing both glass and iron. The presence of iron more than compensated for the beneficial reduction in leach rates observed for most elements in brine. Surface analysis revealed that iron resulted in a greater depth of Cs extraction from the glass than in brine alone, and a reduction in the thickness of the protective Mg-rich surface layer. Shade, Pederson and McVay (1984) also showed that the magnitude of the iron effect is dependent on the ratio of surface area of iron to surface area of glass. A value of 10 for this ratio yielded the largest increase in the leaching rate of boron in brine.

Similar results with iron as discussed above have been found for DWRG under static and flowing conditions in air-saturated deionized water, silicate water, and brine. In the first set of static leach experiments iron coupons and powders were used. The ratio of surface area of the iron to glass was 0.7 for the coupons and 28 for the powders. These results are shown in Figure 3.6. The concentrations of B and the normalized mass loss (based on weighing) were higher for the DWRG leached in the presence of iron than in deionized water alone. In contrast, the Si

FIGURE 3.6. Elemental Concentrations, pH and Normalized Mass Loss Versus Corrosion Time for DWRG in Deionized Water Containing Iron Coupons or Powders

concentration was much lower in the deionized water containing the iron powders than in deionized water alone or deionized water with iron coupons. This is most likely due to the formation of more iron silicate colloids and/or precipitates in the solution with the high surface area iron powders. Formation of precipitates would effectively reduce the Si concentration in solution. Large precipitates would settle from the solution and some would collect in the glass and iron surfaces. Precipitates are found on the glass surfaces as shown in Figure 3.7. Although not shown, precipitates were also observed on the surface of the iron. Jantzen (1983, 1984a, 1984b) has identified the precipitates on a similar glass (SRL-165) leached under oxic conditions in the presence of iron as greenalite (hydrous iron silicate) and iron hydroxides.

SEMs of a control DWRG sample exhibited scattered light precipitates and some apparent crystallization of the outer surface of the leached layer. However, the DWRG experiment involving iron produced a large quantity of amorphous flocculant material, nodular precipitates, and well formed star-shaped crystallites in solution. Comparison of top and bottom views of the DWRG in the interactive experiment showed that much of the flocculant material was deposited on the glass surface by settling, but that the nodular and star-shaped products preferentially formed at the leached surface. Similar corrosion products form on the exposed surfaces of the canister material. Figure 3.6 illustrates that iron enhances the leach rate in ground waters as well as deionized water under static conditions.

FIGURE 3.7. SEM-EDS of DWRG Corroded in Deionized Water Containing Iron Coupons or Powders

The formation of reaction products (either in solution or precipitates) is greatly enhanced by the synergistic silica-iron reactions which occur when glass and iron are present in the same solution under oxidic conditions. Moreover, based on boron dissolution and normalized total mass loss, the higher ratio of iron surface area to glass surface area produced the greater extent of leaching. However, the 40-fold increase in this ratio resulted in only about 2-fold increase in the extent of leaching.

The presence of ductile iron in the deionized water resulted in slightly higher pH values. Solution pH is controlled by the ratios of alkali ions, boric acid and silicic acid. Alkali ions increase pH while silica and boron decrease the pH. The formation of iron silicate colloids removes silica from solu-

tion, reducing its contribution to pH and thus resulting in a net pH increase.

The effects of iron in deionized water flowing at 1.0 mL/h are shown in Figure 3.8. Iron coupons with a surface area equal to three times that of the glass were used in these experiments. In both tests there is an initial increase in the pH during the first several days of exposure. A steady state pH is achieved in both solutions after about 21 days, with the pH of the solution containing the iron being slightly lower. The concentrations of B, Na and Li all exhibit the characteristic trends observed in previous flow experiments. There is an initial rapid increase in their concentrations followed by a gradual decrease to steady state values which are achieved after 21 days. In each case, the steady state concentrations for

(A)

(B)

(C)

FIGURE 3.8. Comparison of DWRG Leaching Behavior in Deionized Water and Deionized Water Plus Iron at a Flow Rate of 1.0 mL/h, Temperature Equal to 90°C and SA/V = 0.1 cm⁻¹. (a) pH versus time, (b) boron concentration versus time, (c) Sodium concentration versus time, (d) Lithium concentration versus time, (e) Silicon concentration versus time, (f) Magnesium concentration versus time, (g) Iron concentration versus time, (h) Aluminum and strontium concentrations versus time, (i) Normalized total mass loss.

(D)

(E)

(F)

FIGURE 3.8. Continued

(G)

(H)

(I)

FIGURE 3.8. Continued

these three elements are greater when iron is present. The Si concentration is not as well behaved as are the B, Na and Li curves. After 21 days it appears that this Si concentration may be slightly higher in the presence of iron, but this difference may not be significant considering the scatter in data. In general, the concentration of Al and Sr exhibit the same trends in the presence of iron as do the B, Na and Li. They achieve steady state concentration after 21 days. However, the concentration of both Mg and Fe continue to increase even after 28 days.

The normalized total mass loss is shown in Figure 3.8i for DWRG in deionized water and deionized water with iron. At all times, the extent of leaching is greater when iron is present. For the purpose of comparison, silicate water data is also included in this figure. Silicate water is effective in reducing the leach rate of DWRG while the presence of iron enhances the leach rate.

Long-term tests involving deionized water, silicate water and silicate water with iron were conducted at a flow rate of 0.1 mL/h. Figure 3.9 presents the results from these

FIGURE 3.9. Comparison of DWRG Leaching Behavior in Deionized Water, Silicate Water and Silicate Water Plus Iron at a Flow Rate of 0.1 mL/h, Temperature Equal to 90°C and SA/V = 0.1 cm⁻¹. (a) pH versus time, (b) Boron concentration versus time, (c) Strontium concentration versus time, (d) Normalized total mass loss versus time.

(B)

FIGURE 3.9. Continued

FIGURE 3.9. Continued

tests. As was found in previous experiments the pH was higher in the presence of iron. Boron and strontium concentrations versus time curves are shown for the three solutions, and they exhibit the characteristic features observed in other flow experiments. Steady state values are obtained in deionized water after about 56 days. However, the concentrations of the two elements continue to decrease even after 112 days in the silicate water and silicate water containing iron. The concentration of Sr approaches the same value in silicate water and silicate water with iron after 56 days, which is significantly lower than in deionized water. Although the Sr concentrations decrease with time, the normalized total mass loss continues to increase with exposure in the silicate water with iron and in the deionized water. In contrast, the normalized total mass loss appears to be leveling off with time in the silicate water.

Table 3.5 summarizes the leaching results (based on normalized total mass loss) for DWRG exposed to various environments. The flow data presented in the table were obtained with the continuous flow test apparatus described in Chapter 1. Both the synthetic silicate water and water from the Stripa mine in Sweden reduce the extent of leaching in comparison to deionized water. However, the presence of iron in the solution increases the extent of leaching in all solutions. This increase in leaching due to iron far outweighed the beneficial effects of the silicate water. The corresponding gel layer thickness occurring under the same corrosion conditions are shown in Figure 3.10. It can be seen that slow flowing waters (i.e., 0.1 mL/h) lead to slightly thicker gel layers than do static waters. Additionally, the presence of silicate water decreases the layer thickness while the presence of Fe increases the thickness. The thickness of the gel layer that forms on DWRG in D.I. water at a flow rate of 0.1 mL/h is the same as on DWRG in silicate water with a flow rate of 1.0 mL/h. This result correlates well with the weight loss data presented in Figure 3.9d and Table 3.5.

The combined effects of water composition, continuous flow and waste package components on the leaching of DWRG under oxic conditions can be summarized as follows:

- a) Leach rates of most elements, and the total normalized mass loss increases as the flow rate increases in all leachants.

- b) Leach rates are generally reduced in silicate water under both static and flowing conditions compared to deionized water.

- c) Leach rates are generally enhanced in the presence of iron under both static and flowing conditions. This is true for deionized water and silicate water. Sr is an exception; under conditions of flow, the reduced steady state leach rate, observed in silicate water is not affected by the presence of iron.

- d) beneficial effects on glass leaching due to silicate water are eliminated in the presence of iron.

Tables 3.6 through 3.12 summarize solution concentrations due to leaching of many of the important elements from DWRG in various leachants with and without ductile iron.

The effects of solution chemistry on the release of Pu, Np, U and several of the major constituents of doped DWRG are summarized in Tables 3.7 through 3.12. (Note that additional information on these same experiments appears in Section 4.5 of Chapter 4. The interactive effects of ground water and iron with waste glass are emphasized in the following discussion; the behavior of the individual radionuclides is emphasized in Chapter 4.) Both silicate water and brine appear to reduce the extent of leaching for most elements in comparison to deionized water. Likewise, the presence of solid iron increases the extent of leaching in deionized water, silicate water and brine.

Pu, Np, U and Sr in leachants containing solid iron appear to be incorporated into filterable colloids since their concentrations are less after filtering (i.e., through 0.45 μ m filter). The concentrations of B and Na are also increased in the presence of solid iron but are not affected by filtering. The presence of iron does not always result in an increase in Si concentrations. Si most likely reacts with the iron to form iron silicate colloids according to the previous discussions. Both the size and compositions of these colloids are probably variable, which could explain the variability of Si concentration when iron is present. Large colloids (or aggregates of colloids) would tend to settle from solution and settle on the surfaces of the leaching vessel as well as the glass and iron surfaces. The Si leached from the glass and precipitated

TABLE 3.5. Normalized Total Mass Loss (based on weighing) for DWRG Under Several Environmental Conditions

Leachant	Flow	Normalized Total Mass Loss (g/m^2)			
		1 month	3 months	6 months	12 months
D.I. Water	0.1 mL/h	5.55	11.89	26.31	47.42
Silicate Water (a)	0.1 mL/h	4.76	6.72	7.68	
Silicate Water + Fe	0.1 mL/h	18.44	19.79	55.63	
D.I. Water	Static	3.62			
D.I. Water + Fe	Static	33.21			
Stripa Water	Static	1.15			
Stripa Water + Fe	Static	27.45			
Silicate Water	Static	2.77			
Silicate Water + Fe	Static	15.71			
D.I. Water	1.0 mL/h	11.90			
D.I. Water + Fe	1.0 mL/h	25.17	60.44		
Silicate Water	1.0 mL/h	5.40			

Experimental parameters: Leached at 90°C , DWRG $\text{SA/V} = 0.1 \text{ cm}^{-1}$, SA of Fe/DWRG $\sim 3/1$; Iron coupons polished to 320 grit prior to being used in the leach tests.

(a) Silicate water used in all experiments is based on Jones' formula (1982).

FIGURE 3.10. Total Alteration Thickness (microns) Versus Leach Time for DWRG Under a Variety of Environmental Conditions. Thickness corresponds to the depth of alteration excluding pits.

TABLE 3.6. Effects of Ductile Iron on DWRG Leach Rates in Dynamic Tests with Ground Water; Monolithic Samples, 90°C

SA/V (m ⁻¹)	Tr (days)	S Fe S glass	Leachant	Leachate Concentration (mg/L)									
				pH	Si	B	Li	Cs	Sr	Ca	Al	Fe	U
0.0			GW	9.71	34.7	0.01	0.00	0.00	0.00	4.88	0.05	0.00	0.00
4.	4	0	GW	9.58	35.4	0.14	0.14	0.011	0.044	4.97	0.25	0.001	0.059
4.	4	2.55	GW	9.89	16.6	0.33	0.29	0.039	0.039	2.22	0.20	6.17	0.041
10.5	28	0	GW	9.40	39.9	0.32	0.34	0.07	0.093	4.59	0.44	0.02	0.28
10.3	28	2.55	GW	10.64	11.4	1.98	2.00	0.48	0.053	1.03	0.62	1.28	0.04

TABLE 3.7. Effects of Solution Chemistry on Release of Pu-239, Np-237, and U from doped DWRG, 56 days, 90°C, Static, SA/V = 0.1 cm⁻¹

<u>Solution</u>	<u>Total</u>	<u>Direct</u>	<u>Acid Stip</u>	<u>Filtered</u>	<u>Iron, ppm</u>
<u>Pu-239, ppb</u>					
D.I. Water	1.00	0.50	0.40	-	-
D.I. Water + FE	16.50	12.0	1.50	1.50	4.00
Brine Solution	0.45	0.33	0.15	0.30	-
Brine Solution + FE	2.10	1.70	0.3	0.05	0.05
Basalt Solution	0.14	0.09	0.05	0.07	
Basalt Solution + FE	5.00	4.50	0.15	0.20	0.10
<u>Np-237, ppb</u>					
D.I. Water	6.00	5.50	0.90	-	-
D.I. Water + FE	19.00	5.00	2.00	2.00	13.50
Brine Solution	2.50	2.00	1.00	1.80	-
Brine Solution + FE	4.40	3.00	0.50	0.50	1.00
Basalt Solution	3.00	2.40	0.75	1.60	-
Basalt Solution + FE	27.00	10.00	2.50	1.00	11.00
<u>U, ppb</u>					
D.I. Water	-	-	-	-	-
D.I. Water + FE	-	-	-	-	-
Brine Solution	0.58	0.04	0.55	0.03	-
Brine Solution + FE	2.25	1.75	0.20	0.05	0.25
Basalt Solution	1.10	1.10	0.03	1.10	-
Basalt Solution + FE	2.00	1.30	0.10	0.07	0.70

TABLE 3.8. Summary of Leach Solution Data from Uranium-Doped DWRG

	D.I. H ₂ O, ppm			D.I. H ₂ O + Fe, ppm		
	14d	28d	56d	14d	28d	56d
B - Leach Solution	2.2	2.54	2.79	3.96	5.3	5.81
Filtered Solution	2.2	2.51	2.81	3.91	5.27	5.75
Acid Strip	(a)	0.029	0.033	0.049	(a)	0.065
Fe - Leach Solution	0.086	0.176	0.023	56.1	80.6	5.72
Filtered Solution	0.85	0.100	0.010	48.6	79.6	0.014
Acid Strip	(a)	0.371	0.072	35.4	(a)	25.6
Na - Leach Solution	7.6	8.82	10.1	14.7	19.3	22.8
Filtered Solution	8.1	8.93	10.4	14.1	19.3	19.7
Acid Strip	(a)	0.109	0.109	0.160	(a)	0.388
Si - Leach Solution	20.2	23.5	25.4	21.5	21.2	19.3
Filtered Solution	20.5	23.3	25.4	20.0	21.1	18.0
Acid Strip	(a)	0.431	0.296	4.0	(a)	2.52
Sr - Leach Solution	0.120	0.104	0.099	0.169	0.176	0.43
Filtered Solution	0.120	0.065	0.030	0.126	0.176	0.001
Acid Strip	(a)	0.044	0.005	0.026	(aq)	0.027

(a) Data not available.

Conditions = 90°C, SA/V = 10 m⁻¹

TABLE 3.9. Summary of Leach Solution Data from Plutonium-Doped DWRG

	D.I. H ₂ O, ppm			D.I. H ₂ O + Fe, ppm		
	14d	28d	56d	14d	28d	56d
B - Leach Solution	1.637 ppm	2.152	2.183	3.452	4.71	6.87
Filtered Solution	(a)	(a)	(a)	(a)	4.83	6.81
Acid Strip	<0.005	0.006	<0.005	0.303	0.227	2.42
Fe - Leach Solution	0.026	0.011	0.046	30.42	7.79	45.8
Filtered Solution	(a)	(a)	(a)	(a)	0.041	0.027
Acid Strip	0.088	0.05	0.056	88.51	196.0	85.3
Na - Leach Solution	4.344	5.506	5.789	10.73	16.0	23.3
Filtered Solution	(a)	(a)	(a)	(a)	15.7	21.3
Acid Strip	<0.1	<0.1	<0.1	<0.1	0.07	<0.02
Si - Leach Solution	16.91	21.83	22.09	13.38	15.1	28.1
Filtered Solution	(a)	(a)	(a)	(a)	14.2	22.3
Acid Strip	0.047	<0.04	<0.04	6.51	9.77	3.57
Sr - Leach Solution	0.119	0.106	0.086	0.108	0.054	0.203
Filtered Solution	(a)	(a)	(a)	(a)	0.002	0.002
Acid Strip	0.002	0.002	<0.001	0.043	0.057	<0.001

(a) Data not available.

Conditions = 90°C, SA/V = 10 m⁻¹

TABLE 3.10. Summary of Leach Solution Data from Neptunium-Doped

	D.I. H ₂ O, ppm			D.I. H ₂ O + Fe, ppm		
	14d	28d	56d	14d	28d	56d
B - Leach Solution	2.11	2.49	2.82	3.90	5.55	7.04
Filtered Solution	(a)	(a)	(a)	(a)	2.63	7.03
Acid Strip	<0.006	0.027	<0.006	0.052	0.241	1.65
Fe - Leach Solution	0.052	0.038	0.021	34.9	12.2	26.1
Filtered Solution	(a)	(a)	(a)	(a)	0.028	0.026
Acid Strip	0.118	0.094	0.159	81.0	100.8	89.6
Na - Leach Solution	6.38	7.49	8.61	13.0	18.6	24.6
Filtered Solution	(a)	(a)	(a)	(a)	10.3	22.5
Acid Strip	<0.02	<0.02	<0.02	<0.02	0.02	<0.02
Si - Leach Solution	19.2	22.4	25.0	16.7	18.7	25.4
Filtered Solution	(a)	(a)	(a)	(a)	7.49	22.0
Acid Strip	0.07	0.46	0.09	10.2	6.49	3.16
Sr - Leach Solution	0.128	0.108	0.102	0.083	0.076	0.128
Filtered Solution	(a)	(a)	(a)	(a)	<0.001	0.001
Acid Strip	0.003	0.006	0.003	0.044	0.066	0.001

(a) Data not available. Conditions = 90°C, SA/V = 10 m⁻¹TABLE 3.11. Summary of Leach Solution Data from Plutonium-Doped DWRG (SGD-PU)
(All concentrations are in ppm) (90°C; SA/V = 10 m⁻¹)

	Basalt Groundwater			Basalt Groundwater + Fe		
	14d	28d	56d	14d	28d	56d
A1 L.S. (a)	0.83 ± 0.05	1.00	1.30 ± 0.10	1.7	2.6	8.9
F.S. (a)	0.81 ± 0.03	0.88	1.20 ± 0.10	0.56	0.87	2.3
A.S. (a)	<0.03	<0.03	0.10 ± 0.03	0.63	0.58	0.57
B L.S.	0.702 ± 0.038	0.761	0.949 ± 0.006	1.85	5.14	10.7
F.S.	0.673 ± 0.016	0.741	0.967 ± 0.016	3.02	4.90	9.7
A.S.	<0.006	<0.006	<0.006	0.084	0.090	0.311
Ca L.S.	2.71 ± 0.20	2.80	2.98 ± 0.14	2.41	2.72	4.5
F.S.	3.02 ± 0.10	2.76	3.12 ± 0.26	0.908	0.757	0.315
A.S.	0.071 ± 0.007	0.024	0.105 ± 0.022	0.741	0.421	0.211
Fe L.S.	0.485 ± 0.030	0.805	0.893 ± 0.020	127.	201.	920.
F.S.	0.070 ± 0.020	0.055	0.044 ± 0.007	0.040	0.051	0.090
A.S.	0.087 ± 0.013	0.046	0.088 ± 0.022	81.5	104.	254.
Na L.S.	320 ± 20	320.	380 ± 30	290.	370.	400.
F.S.	310 ± 20	310.	375 ± 25	320.	360.	380.
A.S.	10.3 ± 0.8	4.4	9.3 ± 2.7	13.	6.8	9.5
Si L.S.	43 ± 4	45.	46 ± 4	37.	38.	92.
F.S.	42 ± 3	42.	44 ± 3	15.	11.	22.
A.S.	0.82 ± 0.08	0.08	0.52 ± 0.26	13.	8.7	8.2
Sr L.S.	0.113 ± 0.004	0.131	0.152 ± 0.002	0.30	0.453	0.865
F.S.	0.094 ± 0.004	0.106	0.127 ± 0.002	0.016	0.013	0.002
A.S.	<0.001	<0.001	0.003 ± 0.002	0.092	0.065	0.026

(a) L.S. = Leach Solution; F.S. = Filtered Solution; A.S. = Acid Strip.

TABLE 3.12. Summary of Leach Solution Data from Neptunium-Doped DWRG (SDG-Np)
(All concentrations are in ppm) (90°C; SA/V = 10 m⁻¹)

		Basalt Groundwater			Basalt Groundwater + Fe		
		14d	28d	56d	14d	28d	56d
A1	L.S. ^(a)	1.09 ± 0.10	0.94 ± 0.16	1.00 ± 0.05	1.90	1.0	4.4
	F.S.	0.83 ± 0.10	1.04 ± 0.15	0.90 ± 0.05	0.50	0.53	0.88
	A.S.	<0.03	<0.03	<0.03	<0.03	0.12	0.32
B	L.S.	0.705 ± 0.016	1.10 ± 0.20	0.933 ± 0.026	2.91	4.10	5.20
	F.S.	0.686 ± 0.016	1.06 ± 0.30	0.906 ± 0.011	2.72	4.10	5.69
	A.S.	<0.006	0.13 ± 0.20	<0.006	<0.006	0.085	0.110
Ca	L.S.	2.69 ± 0.20	2.86 ± 0.20	2.69 ± 0.08	2.42	1.4	2.9
	F.S.	3.02 ± 0.20	2.90 ± 0.20	2.95 ± 0.20	0.964	0.754	0.74
	A.S.	0.06 ± 0.02	0.095 ± 0.040	0.124 ± 0.031	0.08	0.526	0.32
Fe	L.S.	0.595 ± 0.040	0.530 ± 0.080	0.726 ± 0.077	180.	61.1	815.
	F.S.	0.120 ± 0.060	0.065 ± 0.005	0.089 ± 0.046	0.066	0.092	0.087
	A.S.	0.093 ± 0.010	0.100 ± 0.010	0.082 ± 0.009	18.	44.9	200.
Na	L.S.	370 ± 10	360 ± 12	365 ± 5	370.	370.	355.
	F.S.	360 ± 10	370 ± 15	360 ± 10	350.	370.	370.
	A.S.	3.1 ± 0.3	6.5 ± 0.7	9.1 ± 2.9	2.5	3.8	6.3
Si	L.S.	44 ± 4	44 ± 4	44 ± 3	39.	21.	61.
	F.S.	41 ± 4	41 ± 4	42 ± 4	15.	14.	9.1
	A.S.	0.38 ± 0.03	0.40 ± 0.05	0.35 ± 0.10	1.9	3.9	6.2
Sr	L.S.	0.113 ± 0.008	0.124 ± 0.009	0.136 ± 0.004	0.303	0.206	0.88
	F.S.	0.088 ± 0.006	0.102 ± 0.009	0.106 ± 0.006	0.018	0.018	0.005
	A.S.	<0.001	<0.001	<0.001	<0.001	0.083	0.045

(a) L.S. = Leach Solution; F.S. = Filtered Solution; A.S. = Acid Strip.

either back onto the glass or metal surfaces would not show up in solution analysis. The iron silicate colloids must be smaller than the filter size since filtering did not alter the measured Si concentration.

Zeta potential measurements were made on some of the colloids or particles obtained from the flowing solutions. These solutions had pH values in the range of 9 to 9.5. The zeta potential of the colloids from the silicate water containing iron coupons was -37 mv; it was -11 mv for the colloids from the deionized water with the iron coupons. The size of the colloids on which measurements were made was between 0.2 and 0.3 μ m. Colloids of the size necessary for zeta potential measurements (>0.1 μ m) could not be found in the silicate or deionized waters without iron. Iron hydroxide (Fe (OH)₃) has a zeta potential of +14 mv at a pH of 10 (McVay and Buckwalter 1982). The zeta potential of silicate glasses in high pH solutions (Grambow 1982) is greater than -80 mv. The negative silica either in ionic form or as a colloid is

strongly adsorbed to the iron hydroxide surface. Based on the zeta potential measurements of the colloids, their surface chemistry is dominated by silica. The higher zeta potential measured on the colloids in the silicate water with iron coupons compared to deionized water with iron coupons is due to the higher silica concentration in the former solution.

Zeta potential measurements were also made on the DWRG in deionized water. Values of -25 mv to -40 mv were obtained in the pH range of 8.8 to 9.7. However, this negative charge would not prevent the settling of aggregates of iron silicate colloids onto its surface.

Jantzen (1984a) has studied the effects of Eh on the leaching of SRL-165 waste glass. The enhancement of glass leaching in the presence of ductile iron is due to changes in the Eh caused by the presence of iron in aerated water. Fe²⁺ is produced which drives the Eh into a region of stability for iron silicate,

forming either as colloids or precipitates. Oxygen is required for the dissolution of iron as Fe^{+2} . Fe^{+2} then scavenges silica from solution resulting in undersaturation of silica, and thus more dissolution of the glass. Under anoxic conditions, the continuous supply of oxygen required to produce Fe^{+2} will not be available and hence the synergistic effects discussed above should not be observed. Recent results presented by Jantzen (1983, 1984b) show that this is indeed the case. Iron silicate forms under both oxic and anoxic conditions. However, under anoxic conditions where the supply of oxygen is limited, iron silicate forms only on the surfaces of the iron and glass (i.e., not in solution) and this reaction is expected to be self-limiting once a continuous layer is formed on the surface of both components. Colloids are not produced under anoxic conditions due to the limited supply of Fe^{+2} in solution. The surface layers that form under oxic conditions have been shown to be different than those that form under anoxic conditions (Jantzen 1983, 1984a, 1984b). Oxic conditions resulted in a surface film of greenalite and iron oxides. The layers formed under anoxic conditions were more amorphous and less well-defined structures of SiO_2 and iron silicate.

In addition to iron, bentonite has also been shown to accelerate the leaching rate of borosilicate glasses. The mechanisms responsible for the enhanced leaching have not been studied as extensively as have those reported for iron. Currently it is thought that the accelerated attack is due to the ion exchange and sorptive properties of the bentonite. When ions leach from the glass they can be sorbed onto active surface sites on the clay particles. This effectively lowers their solution concentrations and prevents saturation. Undersaturation acts as the driving force for further glass dissolution.

The most extensive laboratory evaluation of glass leaching in the presence of bentonite was performed by Christensen et al. (1984). The presence of bentonite was found to increase the extent of leaching by a factor of 2. This was true when bentonite was in compacted or uncompacted form, although the former form appeared to be slightly more aggressive. Heterogeneous attack was observed on the surface of the glass in contact with the bentonite, as compared to a more uniform attack normally found on glass leached in deionized water. Hench, Werme and Lodding (1982) have studied the effects of bentonite on glass leaching using both laboratory and field tests. In both tests bentonite was found to accelerate the extent of glass

leaching. However, there was less of an effect in the field tests. The magnitude of the effect depends on the ratio of clay to water; it decreases as this ratio decreases. The effect also appears to diminish with exposure time.

Several extensive field studies have been conducted using compacted bentonite interfaced with borosilicate glass (Hench, Werme and Lodding 1982; Werme, Hench and Lodding 1982; Wicks and Ross 1984a, 1984b). These results, which are presented in the following section, are consistent with laboratory tests.

3.6 CORRELATION OF FIELD AND LABORATORY DATA

Few controlled field tests have been conducted and correlated with laboratory tests. One of the earliest field tests was initiated by the Canadians in 1960 (Walton and Merritt 1980; Merritt and Parsons 1964; Merritt 1977; Melnyk, Walton and Johnson 1983). Radioactive nepheline syenite-based glass blocks were buried below the water table in a sandy soil. Release and migration of ^{137}Cs and ^{90}Sr were monitored for 17 years. One of the most significant aspects of this experiment was the comparison of results from the field with those obtained in the laboratory. The observed field leach rate was over 200 times lower than the lowest leach rate reported in the laboratory. The authors attributed about 1/5 of this decrease to the lower aggressiveness of ground water over distilled water (used in the laboratory experiments) and to its lower temperature (6°C in field compared to 25°C in the laboratory). The remaining decrease in leach rate was attributed to the formation of a protective surface layer. Conclusive evidence for this layer was not obtained due to retrieval methods which could have mechanically removed the friable layers.

The most extensive field tests now being conducted involve deep burial (345 meters below surface) in granite in the Stripa mine in Sweden.^(a) Two configurations of samples

(a) Hench, Werme and Lodding 1982; Werme, Hench and Lodding 1982; Wicks and Ross 1984a, 1984b. Also Hench, Lodding and Werme. "Nuclear Waste Glass Interfaces After One Year Burial in Stripa, Part 1, Glass/Glass." To be published. Lodding, Hench and Werme. "Nuclear Waste Glass Interfaces After One Year Burial in Stripa, Part 2, Glass/Bentonite." To be published. L. L. Hench, A. R. Jurgensen, A. Lodding and L. Werme. "Effect of Uranium on Nuclear Waste Glass Surface Behavior." To be published.

are used. One is a 32 mm dia x 35 mm length minican where an alkali borosilicate glass with simulated HLW is cast into stainless steel and 8 glass-steel-glass, glass-glass, and glass-bentonite interfaces are analyzed. The second configuration is the so-called 51 mm dia x 5 mm thick "pineapple slices" which result in 28 interfaces including glass-glass, glass-bentonite, glass-granite, glass-Cu, glass-Ti, glass-Pb, and glass-Pb/Ti. Five different glass compositions are under investigation; two from the SKBF^(a)/Project KBS-UF^(b) program with 9.0% simulated Swedish commercial waste, and three from the SRL^(c)-UF-SKBF/KBS program with 29.8 to 35% simulated U.S. defense waste. A 20-mm center hole is provided in the samples to accommodate a heater rod and the tests are conducted at both 90°C and ambient (8-10°C) mine temperatures. Ground water chemistry is shown in Table 3.2. Based on a permeability of 1.26 L/m²/yr, the flow rate through the bore holes used in these experiments was 0.6 L/yr. The effective SA/V for the glass interfaces is ~5.0 cm⁻¹. This is based on FTIRRS analysis of SA/V dependence of the leaching of the same buried glasses.

After the buried samples are retrieved, they are analyzed with Fourier Transform Infrared Reflection Spectroscopy (FTIRRS), Secondary Ion Mass Spectroscopy (SIMS), Rutherford backscattering and optical microscopy. Post burial solution analysis is difficult in these burial experiments which is the primary disadvantage. An important point of the burial tests of SRL waste glass is that University of Florida, using FTIRRS, showed SRL-165 was better than TDS-131 and that the higher waste loaded glass was the best of the three compositions. This information, along with the greater interactions of the bentonite, show a correlation of lab data with field data.

Figures 3.11 and 3.12, which summarize some of the findings from the in-situ granite burial experiments, are based upon SIMS analyses^(d) and FTIRRS analyses of the glass interfaces (Hench, Werme and Lodding 1982; Werme, Hench and Lodding 1982; Hench, Lodding

and Werme 1984). As many as 15 to 20 elements are measured by SIMS and the resulting compositional profiles are very complicated. The elements in the nuclear waste glasses generally can be categorized as three types: a) mobile ions depleted from the surface without reaching solubility limits; b) mobile ions which reach solubility limits and therefore concentrate in the surface; and c) relatively immobile matrix ions.

The maximum rate of release of a species from a glass surface is exemplified by type (a) ions. Sodium, lithium, and boron behave as type (a) ions. Profiles of boron depletion depths of the "pineapple slice" configuration after a one year, 90°C Stripa burial are compared in Figure 3.11 for various glass interfaces and two glass compositions. Both compositions are similar to the glasses selected by the French for use in commercial waste solidification at La Hague (CEA Group 1982). The boron depletion profile of glass ABS 39 after just 28 days of MCC-1 static 90°C leaching with SA/V = 0.1 cm⁻¹ is shown for comparison in Figure 3.11.

The depletion depths shown in Figure 3.11 range from 0.2 µm to 15 µm depending upon composition and the interface exposed after one year of burial at 90°C. The presence of bentonite increases this depth by a factor of approximately 5x, whereas granite decreases the depletion depth by about 2x. This behavior is attributed to bentonite serving as a semi-infinite ion exchange medium where Ca from the bentonite is replacing Na, Li, and B from the glass (Hench, Werme and Lodding 1982). In contrast, the small congruent solubility of granite seems to augment the glass in reaching solubility limited leaching.^(e)

Clark et al. (1982) have conducted burial tests involving bentonite interfaced with three SRL waste glasses. Their results are consistent with those reported by Hench, Werme and Lodding (1982) and clearly indicate that bentonite accelerated the rate of surface deterioration during the first month of burial (Figure 3.12).

Figure 3.12 also summarizes the time dependence of the boron depletion depth for these experiments using data from 1, 3, and 12 mo. burials. An important finding is the decreasing rate of surface depletion at longer

(a) SKBF: Swedish Nuclear Fuels Supply Co., Stockholm, Sweden

(b) University of Florida, Gainesville, Florida 32611

(c) SRL: Savannah River Laboratories, Aiken, South Carolina

(d) SIMS analysis performed by Professor Alex Lodding, Chalmers University of Technology, Goteborg, Sweden.

(e) L. L. Hench, A. R. Jurgensen, A. Lodding and L. Werme. "Effect of Uraninite on Nuclear Waste Glass Surface Behavior." To be published.

FIGURE 3.11. SIMS Analysis of Buried Samples and One Laboratory Sample of Nuclear Waste Glasses. The depth of leaching corresponds to the depth from which boron was removed from the glass. All samples were exposed to 90°C.

times, similar to the findings of long term laboratory leaching experiments. Consequently, one can use an extrapolation of the 3 mo to 12 mo burial data to predict an upper limit for the depletion depth resulting from leaching during the thermal period (ca. 300 years). If one assumes a worst case of water contact within a breached canister and a constant 1 L/yr flow, as in the Stripa test, throughout an entire 90°C thermal period, it would result in boron depletion of approximately 9 μm for glass ABS 41 and approximately 70 μm for glass ABS 39. Depletion depths would be even less for other elements due to their incorporation in outer reaction layers of the glass (Wicks, Robnett and Rankin 1982). The decreasing slope of the glass-bentonite interfaces, Figure 3.12, indicates that the rapid bentonite ion exchange process will also reach saturation and

will not degrade long term leaching performance of the storage system over just glass-glass interfaces.

Several other points must be considered when using extrapolations of these field test data. Lower SA/V ratios than those achieved in the Stripa burial experiments might be present in an actual breached canister. A comparison of surface profiles from lab studies at $\text{SA/V} = 0.1 \text{ cm}^{-1}$ with 1-yr post-burial data indicates that depletion depths may increase by a factor of 5 to 10x, (Figure 3.11). Studies of SA/V dependence of leaching in the laboratory have shown that as SA/V increases, the depth of surface ion depletion decreases (Pederson et al. 1983), as does the extent of surface deterioration (Figure 3.2). As a consequence, significantly smaller depletion depths are measured

FIGURE 3.12. Boron Depletion Depth Versus Time for Several Nuclear Waste Glasses Exposed to Various System Components. All data was obtained from samples exposed to 90°C.

for the in-situ burial samples which replicate more closely low flow rate repository conditions than samples corroded in the laboratory. There are two primary reasons for the difference: 1) a higher SA/V ratio in the burial experiments and 2) the presence of Si in natural ground waters. Both of these conditions reduce the amount of Si extracted from the glass before solubility limits are exceeded. Figure 3.2 illustrates the beneficial effects of both a high SA/V and the presence of Si in the water prior to contact with the glass.

Another important factor is that use of compacted bentonite in the Stripa burial ensures tightly adherent interfaces due to swelling pressures and therefore more closely simu-

lates high SA/V repository conditions than lab experiments with low SA/V ratios.

The metallic overpacks Pb, Cu and Ti have little effect on the leaching performance of borosilicate glasses buried in granite. This is at least partially due to the ability of these ductile metals to conform to the glass surfaces producing tight interfaces and limiting water accessibility. This physical constraint reduces the extent of leaching required to achieve saturation and hence reduces the leach rate of the glass.

On the conservative side, data from longer term 2 to 3-yr burial samples may result in even lower rates of surface depletion since the slopes of Figure 3.12 may continue to

decrease. Progressively decreasing temperatures during the thermal period will also decrease the rate of surface depletion (Altenheim, Lutz and Ewing 1982). Ambient temperature burial of glasses ABS 39 and 41 show evidence of less than 0.1 to 0.3 μm of surface attack after 1 year. If this slow rate were to continue throughout the 10^5 years of the post thermal period of storage, it would result in an additional depletion depth of at most 1 to 3 cm. The thickness of reaction layers in natural glass analogues exposed to weathering at ambient temperatures indicate that depletion depths of only a few mm or less are more likely. For example, Allen (1982) has shown that a naturally occurring volcanic glass of basaltic composition containing only ~50% SiO_2 and 20% (R_2O , RO)s formed a surface alteration layer <100 μm thick after 10 million years of exposure to water or hydrothermal fluids. Surface alteration is essentially absent even after this extreme time under dry conditions. He concludes that the formation of the clay-like, cryptocrystalline palagonite layer on the glass protects it from further alteration. Data from longer-term nuclear waste glass burial experiments will provide a quantitative base for checking this important conclusion.

It is important to note that the burial tests of simulated SRL HLW waste glasses showed that glass SRL-165 with 30% TDS waste was better than TDS-131 with the same percentage of TDS waste (Clark et al. 1984). Also, it was shown that an increase in waste loading from 30 to 35% increased the performance of TDS-131 glass. These findings, along with the demonstrated effects of bentonite, granite, and metal interfaces, correlate well with the results of lab experiments. Additional experiments are in progress to quantify these burial data in order to use post-burial depletion profiles in predictive equations. However, the presence of bentonite, or other backfill, or overpack, materials, may control the solution chemistry such that SA/V effects are altered in a repository using such components.

3.7 CONCLUSIONS

- In static solutions, the extent of leaching is greater in pure water than in silicate waters.
- In static solutions, the extent of leaching is greater in pure water plus iron than in pure water.

- In static solutions, the extent of leaching is greater in pure water plus iron than in silicate water with iron.
- In both pure water and silicate waters an increase in the flow rate results in a decrease in the solution concentration of most elements exiting the leaching vessel; however, the extent of leaching increases as the flow rate increases.
- Under conditions of flow, the leach rates are lower in silicate water than in pure water; however, as the flow rate increases the differences in leach rates between pure water and silicate water are diminished.
- When iron is present under conditions of flow in either pure water or silicate water the extent of leaching is increased.
- Although ground waters improve the leaching performance of the glass, these beneficial effects are for the most part eliminated when iron is present.
- The extent of leaching obtained on several types of glasses buried in deep boreholes in granite is less than obtained under standard testing conditions in the laboratory. When testing conditions in the laboratory are changed to simulate the burial conditions, results similar to those obtained on the field are obtained. These correlations suggest that the solution composition and high SA/V ratios encountered in the field tests are responsible for the reduced leach rates.
- The presence of stainless steel does not appear to effect glass leaching.
- The presence of bentonite increases the leaching rate of glass, but this effect appears to diminish with exposure time.

3.8 APPENDIX - DISCUSSION OF STATISTICAL ANALYSES

The results from the static experiments reported in this chapter are average values of at least two samples tested under the same conditions. Flow experiments involved more samples in the beginning of tests than at the end. For example, the one year flow test conducted at a flow rate of 0.1 mL/h was started with eight sample cells. Two sample cells were removed from the oven at 1-month, 3-month, 6-month and 12-month intervals.

Thus, during the first month, solutions were collected and analyzed from all eight cells and from these analyses the mean value, $\bar{X}$, the standard deviation, S , and the percent relative standard deviation, %RSD, were calculated. At the end of 1 month, two cells were removed from the oven, and the glasses inside these cells were used to calculate the mean weight loss. Between 1 month and 3 months, six sample cells were used for the solution analyses and after 3 months two more sample cells were removed from the oven in order to analyze the glass samples. This technique was continued until all of the samples were removed from the oven.

Table 3.13 summarizes the %RSD for the various experiments. These values were calculated using the following formulas:

$$\text{Mean, } \bar{X} = \frac{\sum_{i=1}^n X_i}{n}$$

$$\text{Standard Deviation, } S = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}}$$

$$\%RSD = \frac{S}{\bar{X}} \times 100$$

The %RSD normalizes the standard deviations and permits their comparison over time and among experiments. Short term data can produce large %RSD due to the concentrations of some elements being close to the limits of detection. In general, the %RSD decreases as the duration of the experiment increases.

Error bars are indicated in most of the figures in this chapter. These bars represent the range of values obtained for each time period. Error bars are given for random times corresponding to periods in the beginning, middle and conclusion of the experiments.

TABLE 3.13. Average %RSD Between Leachate Samples

Experimental Conditions	Time	pH	Na	Li	Si	B
D.I. Water Static	1 day	3.7	104.	14.1	85.0	15.7
	3 day	2.0	18.7	22.2	117	41.0
	7 day	2.2	14.8	16.7	28.6	26.2
	14 day	1.7	4.7	0.0	26.5	0.0
	21 day	0.6	4.0	0.0	8.31	39.0
	28 day	0.5	4.3	0.0	2.70	22.5
D.I. Water 0.1 mL/h	1 month	2.64	18.3	129.	2.54	42.4
	3 month	1.84	23.6	19.2	21.3	16.5
	6 month	1.15	11.6	11.5	10.2	20.1
	12 month	0.75	13.3	11.9	15.2	15.9
D.I. Water 1.0 mL/h	3 day	12.4	51.6	37.4	74.9	127.
	7 day	22.3	70.5	58.8	70.2	89.5
	14 day	2.77	20.8	15.0	20.2	14.6
	21 day	0.87	9.0	12.0	16.1	14.8
	28 day	1.16	15.7	22.4	12.7	21.8
Silicate Water 0.1 mL/h	1 month	0.43	5.5	43.7	3.4	17.5
	3 month	1.09	7.4	22.4	8.1	22.0
Silicate Water + Fe 0.1 mL/h	1 month	0.8	9.8	44.3	13.2	23.0
	3 month	1.3	15.8	91.8	13.5	54.2
Silicate Water + Fe Static	14 day	6.2	4.8	29.2	56.1	29.4
	28 day	0.1	0.3	14.6	25.8	8.8
Stripa Water Static	1 month	0.6	0.8	4.0	6.5	25.9

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CHAPTER 4
DISSOLUTION OF SPECIFIC RADIONUCLIDES

CHAPTER 4

Dissolution of Specific Radionuclides

ASSIGNMENT: INVESTIGATE THE DISSOLUTION OF LONG-LIVED RADIONUCLIDES FROM WASTE GLASS. BECAUSE THESE RADIONUCLIDES ARE MULTIVALENT, THE INVESTIGATION MUST INCLUDE EXAMINATION OF METHODS TO MEASURE AND CONTROL Eh OF THE LEACHING SYSTEM

SUMMARY: The dissolution behavior of technetium, uranium, neptunium and plutonium from defense waste reference glass was studied. The effect of Eh on the leaching behavior of technetium and uranium was found to be significant because the valence states have different solubilities: e.g., U^{6+} (soluble)/ U^{4+} (insoluble) and Tc^{7+} (soluble)/ Tc^{4+} (nearly insoluble). Special precautions were taken to incorporate technetium in the waste glass as Tc^{4+} in order to obtain a homogeneous distribution of technetium in the glass matrix.

A properly-cleaned platinum electrode was found satisfactory for measuring Eh. Equilibrium redox conditions were found to pertain only at the extreme upper and lower ends of the Eh range, that is, near the upper and lower stability limits of water. Experimentally, the former was obtained by contact with air, the latter by continuous bubbling of forming gas through the leaching system in the presence of a palladium catalyst.

The dissolution of Tc from the waste glass under oxidizing conditions followed a mixed linear-parabolic kinetics and was strongly influenced by the initial pH of the solution. Dissolution of Tc was slowed by several orders of magnitude under highly reducing conditions. Uranium dissolved incongruently under oxidizing conditions but with the same time dependence as the glassforming elements. The ratio of U/B in the leachate varied with pH. The ratio was lowest in the near-neutral pH regimes.

The dissolution behavior of neptunium and plutonium was studied only at high Eh, which should yield the most soluble species. The form of the transuranics leached from waste glass was found to be at least partially associated with colloidal-sized particles (held on a 1.8 nm filter) in almost all tests. With deionized water leachant, the leached transuranics were almost totally filtered out; but with brine leachants the transuranics passed through the filter, showing that soluble species were dominant. Simulated ground water leachants tended to exhibit an intermediate behavior. Leached uranium exhibited a much smaller tendency to be associated with colloidal species than did neptunium and plutonium.

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CHAPTER 4

DISSOLUTION OF SPECIFIC RADIONUCLIDES

4.1 INTRODUCTION

Separate, to some extent, from the question of the breakdown and dissolution of the glass matrix, is the question of the leaching or dissolution of specific elements that are deemed to be of particular importance. Those elements of greatest significance to the long term safety of a defense nuclear waste repository are technetium, uranium, and the transuranic elements.

Technetium, uranium and the transuranic elements, with their long half lives, are the major radionuclides from the waste that survive well into the 'geological' time period of the repository. The sections that follow discuss experimental results on the dissolution of these elements from the MCC reference glass.

4.2 OXIDATION POTENTIALS IN GLASS DISSOLUTION

Many radionuclides of importance in nuclear waste management occur in more than one valence state. Usually the valence states have different solubilities [e.g., U^{6+} (soluble)/ U^{4+} (insoluble) and Tc^{7+} (soluble)/ Tc^{4+} (nearly insoluble)]. The long-term leaching behavior of waste forms will be a function of the stable valence states of the various radionuclides.

Reactions connecting different valence states require an exchange of electrons in the same way that acid-base reactions require an exchange of protons. Since most waste forms are oxides, these reactions can be described by oxidation potentials. In a complex system such as a nuclear waste, there are many reactions under way simultaneously. If the system is to be at equilibrium (a situation that is seldom obtained), all of these must be adjusted to a single oxidation potential which may be regarded as a system master variable.

Lindberg and Runnells^(a) analyzed 611 ground water analyses for which a measured Eh and at least one analyzed redox couple was present. They reached the conclusion that no meaning-

ful statement can be made about redox potential in low ionic strength ground waters because all of the pertinent reactions are out of equilibrium. Although Eh can be measured, the relationship of the number obtained to any redox reaction in the solutions is problematic at best. The analogy between Eh and pH breaks down, these authors argue, because there is no free electron in solution to act as an intermediary in redox reactions the way in which the free proton acts as the intermediary in acid-base reactions.

The extent to which nuclear waste dissolution reactions are controlled by Eh is still open to debate in spite of some fairly intensive research over the past several years. It will be shown in this report that Eh plays an important role in the dissolution behavior of both technetium and uranium. The extent to which these effects can be described quantitatively and incorporated into rate equations is still open.

4.2.1 Concepts and Definitions

Redox equilibria are described in some detail by Garrels and Christ (1965) and Stumm and Morgan (1981). The short section that follows sets out the needed equations and definitions.

Redox potential is usually described by Eh, a macroscopic parameter related to the electron activity. Consider the analogy to pH,

$$pH = -\log [H^+] \quad (4.1)$$

An equivalent parameter can be defined for electrons.

$$pe = -\log [e^-] \quad (4.2)$$

(a) R. D. Lindberg and D. D. Runnells. "A Critical Analysis of the State of Equilibrium of Redox Reactions in Ground Waters, Applied to Eh Measurements and to Geochemical Modelling." *Science* (in press).

If the redox reaction is written as an oxidation reaction, then

$$E_h = \frac{2.303 RT}{F} \text{pe} = -\frac{\Delta G_R}{nF} \quad (4.3)$$

which connects the electrochemical quantities of pe and Eh to the thermochemical quantity of Gibbs free energy of reaction. Since

$$\Delta G_R = \Delta G_R^\circ + RT \ln K \quad (4.4)$$

The equation for Eh can be related to the equilibrium constant

$$E_h = -\frac{\Delta G_R^\circ}{nF} - \frac{RT}{nF} \ln K \quad (4.5)$$

The standard free energy of reaction can be related to a standard electrochemical potential

$$E^\circ = -\frac{\Delta G_R^\circ}{nF} \quad (4.6)$$

This leads to the usual expression for the Nernst Equation

$$E_h = E^\circ + \frac{RT}{nF} \ln \left[\frac{\text{oxidation products}}{\text{reduced reactants}} \right] \quad (4.7)$$

which serves as the usual working definition for Eh.

In the above equations n = number of electrons exchanged, F = Faraday constant (96.487 kJ V⁻¹ mole⁻¹ or 23.062 kcal V⁻¹ mole⁻¹) and R = gas constant = 8.3143 J K⁻¹ mol⁻¹.

Redox reactions pertinent to nuclear waste materials and nuclear waste repositories are likely to take place in aqueous solution or in an aqueous environment. In this case there is a direct connection between Eh and pH. The redox potentials and hydrogen ion activities must also be in equilibrium with the reduction and ionization of water.

$$\begin{aligned} H_2O &= H_2 + \frac{1}{2} O_2 \\ f_{H_2} \cdot f_{O_2}^{1/2} &= 10^{-41.55} \quad (25^\circ C) \quad (4.8) \end{aligned}$$

$$\begin{aligned} H_2O &= H^+ + OH^- \\ [H^+] [OH^-] &= 10^{-14.00} \quad (25^\circ C) \quad (4.9) \end{aligned}$$

Both equations are written at unit activity of H₂O. When these equations are combined through the Nernst Equation, we obtain

$$\begin{aligned} \frac{1}{2} \log f_{O_2} &= \frac{E_h F}{2.303 RT} \\ &+ 2 \text{pH} + \log [H_2O] - 41.55 \quad (4.10) \end{aligned}$$

which connects the oxygen fugacity (often called the 'oxygen partial pressure') with Eh and pH. Thus three system parameters for aqueous environments are linked and specification of any two of them permits calculation of the third.

The reactions described by the equations above also put limits on the stability of liquid water. If Eh - pH conditions are such that either f_{O₂} > 1 or f_{H₂} > 1 at atmospheric pressure, then oxygen or hydrogen gas will be released. Many metals cannot be in equilibrium with liquid water. Iron, for example, will reduce water, become oxidized, and release hydrogen gas. Increasing the system pressure to the several hundred bar values expected for a sealed repository will shift these equilibria, but not by much.

4.2.2 Measurement of Eh

Eh is measured with respect to the standard hydrogen electrode. The reaction H₂ + 2H⁺ + 2e⁻ gives an equilibrium constant equal to unity by definition.

$$K = \frac{a_{H^+}^2}{p_{H_2}} = 1 \quad (4.11)$$

The hydrogen electrode can be achieved experimentally by using a fresh platinum surface in contact with the aqueous solution. The fresh platinum surface is easily poisoned either by oxidation or by adsorption. Care must be taken to avoid supersaturated solutions from which substances can be catalytically precipitated onto the electrode surface. We have found that platinum electrodes continue to function properly after exposure to dilute, undersaturated solutions for more than one month. Platinum metal is not stable in equilibrium with the oxygen pressure of the atmosphere: there is a tendency for spontaneous oxidation of the metal surface (Jantzen 1984). Should oxidation occur, the oxide layer can be removed by light mechanical buffing or by heating the electrode in a hydrogen flame. With these caveats in mind, the platinum electrode can measure Eh in the

sort of aqueous solutions used in dissolution experiments on radioactive wastes.

The measurement configuration consists of the platinum electrode and some reference electrode connected to the millivolt input of a standard pH meter. The Eh is simply the meter reading corrected for the reference electrode potential.

$$E_h = E(\text{meter}) + E(\text{ref})$$

where $E(\text{ref}) = 0.244$ V for the saturated calomel electrode and 0.199 V for the Ag/AgCl electrode at 25°C .

4.2.3 Control of Eh

Separate from the question of the measurement of Eh and the question of whether the measurement has any thermodynamic significance once measured, is the question of control of Eh. Nuclear waste research would benefit if it were possible to conduct dissolution experiments at constant Eh. Leach tests carried out in tightly capped bottles (e.g., as in the MCC-1 procedure) are free-drift experiments with respect to Eh. Free oxygen dissolved in the leach solution and from the air trapped in the bottle is consumed in redox reactions with the waste form and Eh drifts downward away from the oxygen saturation line. Measurements on the MCC Defense Waste Reference Glass (DWRG) gave Eh values of $+0.65$ V at a pH of 3.2 (started at pH 2), before entry of oxygen drove Eh and pH to $+0.7$ and 3.0 respectively. For PNL 76-68 glass, the corresponding experiment resulted in an Eh and pH of $+0.52$ and 4.3 before returning to $+0.60$ and 3.1 .

Jantzen (1984b) examined the Eh that resulted when SRL-165 glass, and crushed basalt were reacted with deoxygenated water. In general, the Eh was lowered to values appropriate to the ferrous/ferric iron ratio present in the material. She found that crushed basalt would reduce Eh to -0.42 volts at a pH of 8.44 in reasonably good agreement with the values of -0.4 volt at pH $= 9.1$ calculated from the chemical composition of the basalt. Jantzen (1984) suggests that addition of crushed basalt is useful for producing conditions of reduced Eh in laboratory dissolution experiments.

Substances added to the system to control Eh should not themselves participate in any of the redox reactions of which they are not already a component. Safest of these is to

keep the solutions in free contact with air thus locking the system on the $P_{O_2} = 0.21$ atmosphere isobar and to expose the solutions to pure hydrogen ($P_{H_2} = 1$) or forming gas (5% H_2 in N_2 ; $P_{H_2} = 0.05$ atmospheres). These Eh controls have the advantage of ease in experimental handling and freedom from extraneous reaction effects. They have the disadvantage that the reaction of molecular oxygen and hydrogen in aqueous solutions is extremely sluggish and may be outrun by other redox reactions in the system. We have found that molecular oxygen reacts fast enough to be useful on the time scale of the usual leach experiments but that hydrogen is essentially inert on this time scale. We have found that the addition of a platinum or palladium catalyst greatly accelerates the reaction and allows reactions at Eh values near the lower stability limit of water.

The behavior of oxygen and hydrogen as redox buffers was investigated using the system Fe-O-H as a convenient and well-known example. Figure 4.1 presents an Eh-pH diagram for the Fe-O-H system using $Fe(OH)_3$ as the insoluble solid species. The Eh as a function of pH for air-saturated solutions and forming gas-saturated solutions is shown by dashed lines.

Solutions of ferric chloride (0.001 molar) in HCl (pH $= 2$) were prepared from reagent grade chemicals. About 25 catalyst pellets (Alfa Products, 0.5% Pt on alumina) and 200 mL of solution were loaded into a 250 mL three-necked flask. In the three necks were inserted a gas bubbler, a combination pH electrode, and a platinum electrode. Commercial forming gas was passed through a bubble tower filled with the same ferric chloride in hydrochloric acid solution before entering the experimental vessel. The electrodes were checked before the start of the experiment and after its conclusion with commercial pH buffers and Zobell's solution.

Figure 4.2 shows the Eh/time plot for the reduction of ferric chloride at 25°C . The flow rate of the forming gas was about 1 mL/second, enough to completely reduce all of the iron in a few minutes if the reaction was not kinetically limited. The highest Eh observed was $+0.85$ in the initial solution. Eh dropped to $+0.80$ rather quickly and then drifted slowly downward for the next 40 hours, after which it dropped precipitously to values near -0.08 . At pH $= 2$ the final Eh values fall exactly on the calculated equilibrium line for forming gas as shown by the lower point on Figure 4.1.

FIGURE 4.1. Eh-pH Diagram for the System Fe-O-H Derived from Thermochemical Data (Naumov, Ryzhenko and Khodakovsky 1971). Heavy lines are phase boundaries. Light lines are molar concentration contours of dominant species. Dashed lines represent Eh-pH relations of air (upper line) and forming gas (lower lines).

FIGURE 4.2. Reduction of FeCl_3 by Forming Gas Over Platinum Catalyst

Figure 4.3 shows the ratio of ferrous to total iron calculated from the Eh. There is a continuous rise in the ferrous iron concentration until the solution is completely reduced after about 40 hours. The small break in slope where the curve becomes flat corresponds to the dramatic drop on the Eh curve. This demonstrates that the reduction is a

FIGURE 4.3. Change in Ferrous Iron to Total Iron Ratio During Reduction of FeCl_3 . Complete reduction occurs in about 40 hours.

steady process and that the spectacular change in Eh is a consequence of the relationship between Eh and the fraction of ferrous iron

$$\frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Fe}^{3+}} = \frac{1}{1 + \exp \left[\frac{nF}{RT} (E_H - E_H^0) \right]} \quad (4.12)$$

Figure 4.3 also demonstrates that the platinum catalyst is effective against molecular hydrogen and that the forming gas will indeed control the Eh.

Figure 4.4 shows the reverse experiment. The flow of hydrogen was turned off and oxygen was allowed to diffuse into the flask around the electrodes. The initial change of

FIGURE 4.4. Eh Changes on Reoxidation of Ferrous Chloride Solution by Admission of Atmospheric Oxygen

Eh is very rapid, rising from -0.1 volt to +0.7 volts in a few hours. After the initial rise, the Eh curve quickly flattens off and slowly drifts upward to reach the starting Eh of +0.85 volts only after 32 days at which time the solution was completely reoxidized. Figure 4.5 shows the ratio of ferrous to total iron. Again there is a steady drop in ferrous iron over the entire 32 day period. The initial rapid rise of Eh is an artifact of Equation 4.12, there being a very rapid change in the $\text{Fe}^{+++}/\text{Fe}^{++}$ ratio when the first small amount of oxygen enters the system.

Figures 4.2 and 4.4 illustrate the difficulty in following redox reactions by Eh measurement. In certain regions, Eh is quite insensitive to changes in valence state ratios whereas in others it is overly sensitive. The initial rapid rise in Eh on oxidation presents an experimental difficulty. If a test solution from an experiment in highly reducing conditions is opened to the atmosphere, there may be considerable Eh drift from introduction of atmospheric oxygen during the short time required to make the measurements. Note that the rapid initial change in Eh takes place with only a small increase in the ferric iron concentration. Complete reaction with oxygen gas is very sluggish; 40 days are required for complete reaction.

The use of an inert sparge gas does not constitute an Eh control by itself unless some other Eh control is present. In the limit of the hydrogen fugacity becoming zero, the Eh is undefined but is positive and large. Applying the same argument for oxygen yields the conclusion that the Eh should have a very large negative value.

FIGURE 4.5. Change in Ferrous Iron to Total Iron Ratio During Reoxidation of Ferrous Chloride Solution

Compounds which are not stable under the conditions of the experiment cannot be used as part of a buffer system to control the Eh. For example, hydrazine is known for being a powerful reducing agent and would seem to be useful to study low Eh conditions. If however, the hydrogen fugacity (or Eh) is calculated with hydrazine present at values near that of its vapor pressure, the hydrogen fugacity is found to be substantially greater than one atmosphere. A similar result is obtained for formaldehyde. A slightly different situation is found for metallic iron or pure chlorine gas; they are stable phases, but they are not stable with water at one atmosphere pressure and room temperature.

The results of the experiments described here and the results of Jantzen's extensive experiments both agree that Eh is not as elusive a variable in nuclear waste reactions as had been previously believed. Further, it does not appear that the pessimistic conclusions of Lindberg and Runnells^(a) apply completely to nuclear waste reactions. This is in large part due to the dominant role of iron as a redox reaction in both nuclear waste reactions and in reactions of ground water with the repository wall rock. The reaction kinetics of ferrous/ferric iron are reasonably rapid. Lindberg and Runnells' results do sound a proper note of caution: Each redox reaction in a nuclear waste dissolution experiment must be evaluated separately. There is no evidence as yet that all such reactions would be in simultaneous equilibrium. The burden lies with the investigator to demonstrate that the redox reactions of interest are at internal equilibrium.

4.3 THE DISSOLUTION OF TECHNETIUM

Technetium-99 is a long half-life (2.12×10^5 years) fission product isotope with a yield of 6.1% from the thermal fission of ^{235}U . At the close of the 1000-year 'design' period of the nuclear waste repository, technetium will be one of the most important sources (68%, 13.3 Ci/MTHM) of remaining activity (Bartlett et al. 1976).

Little is known of the behavior of technetium in waste repositories or of its stability in waste forms. The fully-oxidized state mainly

(a) R. D. Lindberg and D. D. Runnells. "A Critical Analysis of the State of Equilibrium of Redox Reactions in Ground Waters, Applied to Eh Measurements and to Geochemical Modelling." *Science* (in press).

forms covalently-bonded compounds which would not fit the available sites in radiophase ceramics and might not dissolve properly in glass. The intermediate valence Tc^{4+} , however, should substitute into spinel, perovskite, or related phases containing tetravalent ions in nuclear waste ceramics and should dissolve in borosilicate glasses much as do titanium or zirconium. Technetium is a weak beta-emitter (0.246 MeV) and can be handled under glove-box conditions. However, the radioactivity has inhibited much experimentation with technetium in waste forms. Further, unlike nearly every other fission product element, technetium has no nonradioactive chemical simulant. Although it lies between manganese and rhenium on the periodic table, its chemistry is sufficiently different from either of these elements with regard to redox reactions that experiments must be done on the element itself.

4.3.1 Stability of Technetium Species

Relatively few thermochemical data are available for the oxides of technetium, or their ternary compounds, although some values at 25°C have been published (Lavrukhina and Pozdnyakov 1970; De Zoubov and Pourbaix 1966). There is evidence for Tc^{6+} and Tc^{3+} species in aqueous solution (Rulfs, Pacer and Hirsch 1967). Tc_2O_7 is volatile and boils at 310°C. TcO_2 is much more stable and although slightly volatile above 900°C it can be fired under proper oxygen partial pressures to temperatures of 1100°C (Muller, White and Roy 1964). It was found that an oxygen partial pressure of 4×10^{-6} was sufficient to reduce technetium to the Tc^{4+} state over the temperature range of 400-900°C. An oxygen pressure of 10^{-11} atmospheres would reduce the oxide to the metal at 900°C. These experiments bracket the range of oxygen fugacities needed to synthesize technetium-containing waste forms with the more easily incorporated Tc^{4+} ion.

Figure 4.6 shows an Eh-pH diagram for the Tc-O-H system. This diagram was calculated from the thermochemical data tabulated by Zoubov and Pourbaix (1966). Although new data are available for the enthalpy of formation of the pertechnetate ion (Gayer, Herrell and Basey 1976), it was not deemed sufficient to attempt a reestimation of the other thermochemical data. The diagram in Figure 4.6 differs in some detail from that published by Brookins (1978) partly because of the choice of reactions and also perhaps because of the choice of thermochemical data. Brookins was concerned with the role of sulfides in immobilization of radionuclides escaping from the Oklo natural reactor;

FIGURE 4.6. Eh-pH Diagram for the System Tc-O-H. Dashed lines indicate the stability limits of liquid water at 25°C. Heavy lines are phase boundaries between solid phases. Light lines are boundaries of TcO_4^- at the molar concentrations given. Calculated from data in De Zoubov and Pourbaix (1966).

our concern is with the reduction of technetium to the metal in the nuclear waste repository. Technetium metal is stable in the presence of water so long as the Eh-pH conditions are held below the Tc/TcO_2 boundary. The principal oxidation reaction is

Three reaction lines are shown for $[TcO_4^-]$ + 10^{-10} , 10^{-8} , and 10^{-6} molar which correspond approximately to 0.01, 1, and 100 mg/L which is the range of technetium concentration seen in the dissolution experiments. $HTcO_4$ is strong acid. The dissociation reaction

takes place at $pH = -0.12$ and $HTcO_4$ does not appear on the diagram as a dominant species. There is considerable evidence for other species including those containing Tc^{3+} and Tc^{6+} (Cartledge 1971). The Eh-pH diagram for the Tc-O-H system is doubtless much more complicated than is indicated in Figure 4.6.

4.3.2 Preparation of Technetium-Containing Glass

It was necessary to add technetium to the DWRG. This was accomplished by remelting the glass with TcO_2 in a sealed container to prevent the oxidation and volatilization of the technetium. TcO_2 was prepared from NH_4TcO_4 (obtained from Oak Ridge National

Laboratory) by heating at 100°C for 2 hours to decompose the pertechnetate and then at 750°C for 5 hours to dehydrate the dioxide. This procedure results in phase-pure TcO_2 .

A 4-cm-long by 0.45-cm-diameter MCC glass rod was sealed in a 0.5 cm platinum tube together with 0.25 wt% technetium oxide. The platinum tube was sealed in a silica tube, and the assembly was heated in a silica-lined horizontal tube furnace at 1050°C. Higher temperatures or higher technetium oxide contents caused rupture of the platinum tube with the consequent loss of TcO_2 before it had time to dissolve in the glass. The silica tube was rotated for 5 minutes every 1 hour during a total melting time of 20 hours. After cooling in a flow of cold air, the platinum was peeled off the glass rod.

The technetium content was determined by dissolving 0.0184 gm of glass in 10 mL of HF, diluting with 100 mL of HCl solution (pH 1.0), and then neutralizing with calcium hydroxide. One mL of this solution was counted using a beta-scintillation technique. The technetium content was determined to be 0.2 wt% of the glass. An autoradiograph of a glass rod cross-section showed a uniform radial distribution of technetium in the structure (Figure 4.7). In addition, autoradiographs from both ends of the rod indicated a uniform axial distribution as well. The measured bulk density (by pycnometer using alcohol as the fluid) was 2.78 g/cm³. The powder x-ray diffraction pattern of the glass

FIGURE 4.7. Autoradiograph Showing the Uniform Distribution of Technetium Over the Cross Section of Glass Rod. Scale: 1 cm = 1 mm.

showed a completely amorphous phase with no evidence for crystallization.

4.3.3 Dissolution of Technetium Under Oxidizing Conditions

The dissolution of technetium-containing borosilicate glass was studied in a series of 17 experiments. Most of these experiments were performed on crushed glass to increase the surface area and to produce measurable concentrations of ions in the solutions. One experiment was conducted on a bulk piece of glass which was used for surface analysis. The surface area to volume ratios are shown in Table 4.1.

In all experiments, solid was added to 50 mL of aqueous solution. At sampling time, 1 mL of solution was taken for analysis, acidified with 1 drop of concentrated HCl, stored, and then analyzed by DC plasma atomic emission spectroscopy for all elements except technetium. An additional 0.25 mL of solution was added directly to the scintillation fluid and radioassayed for technetium. Because of limitations on the supply of technetium-containing glass, only one set of experiments were performed. The error in counting statistics is about equal to the size of the symbols on the graphs. The duration of most of the experiments was between 40 and 60 days. The pH drifted from initial values because of consumption of protons during dissolution. Table 4.2 gives the final pH values.

Figures 4.8 through 4.10 show the concentration versus time plots for technetium in solutions at initial pH values of 1.0, 3.0 and 11.0. The dissolution kinetics are clearly dependent on the temperature and pH of the solutions. As expected, dissolution rates are higher in strongly acidic and basic solutions than in near-neutral solutions.

TABLE 4.1. Calculated Surface Area to Volume Ratios Used in the Glass Dissolution Experiments

pH	Weight of Glass, g	SA/V cm ⁻¹ (a)
All experiments at pH 1.0, 3.0, and 11.0	0.1	0.29
All experiments at pH 5.6	0.05	0.47

(a) Based on spherical grain approximation.

TABLE 4.2. Initial and Final pH Values of the Solutions Used in Glass Dissolution

Temperature, °C	Initial pH	Final pH ^(a)
90	1.0	0.9
	3.0	3.0
	5.6	8.5
	11.0	9.6
70	1.0	1.0
	3.0	3.1
	11.0	9.6
40	1.0	1.0
	3.0	3.1
	5.6	5.9
	11.0	10.1

(a) All values are the average of several readings.

FIGURE 4.8. Technetium Concentration Versus Time Plot for the Dissolution of Borosilicate Glass in pH 1.0 Solutions at 40, 70 and 90°C

FIGURE 4.9. Technetium Concentration Versus Time Plots for the Dissolution of Borosilicate Glass in pH 3.0 Solutions at 40, 70 and 90°C

The effects of temperature can be clearly seen at pH 1.0 in Figure 4.8. In pH 3.0 solutions (Figure 4.9), the dissolution rate was higher at 70°C than at 90°C. This is thought to be the result of a high initial burst at 70°C. Similar bursts can also be seen at 70°C in pH 11.0 solutions (Figure 4.10). Here, however, the dissolution at 90°C was high enough to eliminate the effect of the initial burst at 70°C. In a pH 5.6 solution at 40°C the concentration of technetium was below the detection limit.

The kinetics and mechanism of glass dissolution are rather complicated. The dissolution starts with linear kinetics which lasts between 2 and 6 days, depending on the temperature and pH of the solutions. This is followed by a region of parabolic kinetics. These two regions are shown in the data for deionized water (Figure 4.11).

Figure 4.12 shows the concentration versus time plot for Si, Na, U, Al, Li, B, and Ca.

FIGURE 4.10. Technetium Concentration Versus Time Plots for the Dissolution of Borosilicate Glass in pH 11.0 Solutions at 40, 70 and 90°C

FIGURE 4.11. Technetium Concentration Versus the Square Root of Time Plot for the Dissolution of Borosilicate Glass in Deionized Water at 90°C

FIGURE 4.12. The Concentration of Si, Na, U, Al, Li, B and Ca Versus Time Plots for the Dissolution of Borosilicate Glass in pH 1.0 Solutions at 90°C

The smooth transition from linear to parabolic kinetics suggests that there is only one dissolution mechanism, which begins with a rapid initial kinetics and slows down as the reaction proceeds. As soon as the glass starts to react with the aqueous solution, it forms a surface layer which increases in thickness with time. The linear kinetics part of the dissolution curve corresponds to a nonprotective layer. As the layer thickness increases, the kinetics slows down and shifts to a parabolic region, because of the diffusive barrier layer.

The surfaces of a leached sample and an unleached sample were profiled by secondary ion mass spectroscopy to examine concentration versus depth. A small cylindrical glass sample with a surface area of 1 cm² and a weight of 0.2 g was dissolved in pH 5.6 solution (100 mL deionized water) for 60 days.

Figures 4.13 through 4.16 compare the depth profiles for unleached and leached surfaces of technetium-containing borosilicate glass that were fractured and profiled. Oxygen is used as a reference in all cases. Figure 4.13 shows a slight build up of H and depletion of Na and Li at the surface of the unleached sample. This could be the result of surface reaction with air moisture. In the leached sample Na and Li are depleted from a 50 nanometer surface layer. However, B, Ba, and Al are accumulated in the same layer. Hydrogen also has a higher concentration in this layer, as it diffuses from the water to replace the leached ions. Figure 4.16 shows that the alkali metal Cs, the alkaline earths Sr and Ba, the transition metals Fe, Zn, Zr, and Tc, and the actinide U are all depleted in the same 50 nanometer surface layer. The silica- and alumina-rich layer seems to act as a reaction barrier, which protected the bulk glass and produced the very thin surface layer shown in Figures 4.15 and 4.16.

4.3.4 Dissolution of Technetium Under Reducing Conditions

The effect of reduced oxygen potential on the leaching of technetium from borosilicate

FIGURE 4.13. SIMS Depth-Profile for Unleached Technetium-Containing Borosilicate Glass Surface (elements with $A < 40$)

FIGURE 4.14. SIMS Depth-Profile for Unleached Technetium-Containing Borosilicate Glass Surface (elements with $A > 40$)

FIGURE 4.15. SIMS Depth Profile for the Surface of Technetium-Containing Borosilicate Glass Leached in DI Water for 60 Days at 90°C (elements with $A < 40$)

FIGURE 4.16. SIMS Depth Profile for the Surface of Technetium-Containing Borosilicate Glass Leached in DI Water for 60 Days at 90°C (elements with A > 40)

glasses was investigated. The aqueous solutions in which glass was dissolved were isolated from the air and forming gas (95% N₂ and 5% H₂) was bubbled continuously through the solution.

The Eh of the solutions was measured four to five times during the first 30 days of the experiment using a platinum electrode and Ag/AgCl reference electrode with saturated KCl. Figure 4.17 shows the range of variation of Eh at every pH; the pH values are the final values. In all cases the Eh values were at or below the region where TcO₂ appears as a dominant species. However, at pH 1.0 the Eh was in the region where residual TcO₄⁻ was still in solution. Figure 4.18 through 4.20 give the concentration versus time plots for the dissolution of technetium containing borosilicate glass in oxidizing and reducing conditions. The effect of reduced oxygen activity is to reduce the leaching of technetium by factors of 1, 4, and 2 at pH 1.0, 3.0, and 11.0 respectively. These factors are in rough agreement with the Eh ranges in Figure 4.17. The Eh values measured, however, suggest that the system is not at equilibrium. Reduction reduces the dissolution rate but the rate may not be adjusted to the measured Eh.

FIGURE 4.17. Eh-pH Diagram for the System Tc-H₂O Showing the Ranges for the Dissolution of Borosilicate Glass Experiments in Forming Gas Atmosphere. (Diagram adapted from Figure 4.6.) Light lines are boundaries of TcO₄⁻ at the molar concentration given.

FIGURE 4.18. Technetium Concentration Versus Time for the Dissolution of Borosilicate Glass in Air and Forming Gas Atmosphere (reduced) in pH 1.0 Solution at 70°C

FIGURE 4.19. Technetium Concentration Versus Time for the Dissolution of Borosilicate Glass in Air and Forming Gas Atmosphere (reduced) in pH 3.0 Solution at 70°C

FIGURE 4.20. Technetium Concentration Versus Time for the Dissolution of Borosilicate Glass in Air and Forming Gas Atmosphere (reduced) in pH 11.0 Solution at 70°C

In one experiment, Pd-coated alumina pellets were added to the solution in which forming gas was continuously bubbled. The experiment was conducted in pH 11.0 solution at 70°C.

The studies of Eh measurement show that this combination produces Eh values near the lower stability limit of water. Another experiment was run simultaneously with an oxygen potential equal to that of the atmosphere. After 33 days the volume of the solution in the reducing environment had decreased to 25 mL (starting with 50 mL). The forming gas and Pd catalyst were removed and the experiment was allowed to continue for another 6 days. The technetium concentration versus time plots for the experiments in reducing and oxidizing solutions are shown in Figure 4.21. In reducing solution there was almost no technetium in solution after 33 days. EDX analysis of the pellet surface gave no evidence for precipitated technetium. The analyses for other elements in the glass showed no detectable difference between oxidizing and reducing conditions.

4.4 THE DISSOLUTION OF URANIUM

Uranium is present in the DWRG at the 2.6% level. Dissolved uranium in borosilicate glasses is known from the work of Schreiber and his students (Schreiber and Balazs 1982) to exist in the U^{4+} , U^{5+} , and U^{6+} valence states. There are complex equilibria among the uranium species which depend on melting temperature and oxygen fugacity for uranium in an inert base glass and also on the concentrations of other variable valence ions in the glass (Schreiber et al. 1982; Schreiber

FIGURE 4.21. Technetium Concentration Versus Time for the Dissolution of Borosilicate Glass Under Oxidizing and Reducing Conditions (forming gas + Pd catalyst) in pH 11.0 Solution at 70°C

et al. 1983; Schreiber, Balazs and Kozak 1983). Hexavalent uranium is thought to be present as the uranyl ion while U^{+5} and U^{+4} exist in 6-fold and 8-fold coordinated sites.

The dissolution of uranium will depend on the oxidation potential of the environment as well as on the valence state available in the glass. According to the Eh-pH diagram of Langmuir (1978), an oxidizing environment should stabilize the uranyl ion at pH 0 to 5. In neutral and basic solutions, uranyl hydroxy complexes would predominate, decreasing the solubility of uranium. Carbon dioxide in solution produces carbonate complexes in the same neutral to basic pH range. Carbonate species are known to enhance uranium solubility (Morse et al. 1984).

4.4.1 Experimental Procedures

Sections of the glass bars were crushed to provide glass fragments in the size range of 350 to 700 μ m with fresh fracture surfaces. The dissolution experiments were a form of static test. Bottles containing glass and solution were maintained at constant temperature and sampled at two-day intervals. The kinetics of dissolution were followed by the uptake of various elements in the sample solutions.

One of the objectives of the study was to determine the effect of pH on glass dissolution. To this end, four leach solutions ranging from an initial pH of 1 to 11 were used. Each solution/glass combination was run at 40, 70 and 90°C and each pH/temperature combination was run in triplicate.

Specific procedures were as follows: The crushed glass was ultrasonically cleaned in acetone and then sieved to provide the correct size fraction. Glass samples weighing 6.22 grams were placed in 100 mL of solution contained in new nalgene bottles that had been previously rinsed with acid. The samples were kept in solution for 75 days. One-mL solution samples were extracted after 24 hours and then every two days for a total of 20 samples followed by weekly samples for 5 weeks. The solution samples were analyzed for uranium on a Scintrex uranium analyzer which allows detection down into the ppb range. All other elements were analyzed simultaneously using a Spectraspan III DC plasma atomic emission spectrometer.

The pH was found to drift rapidly and, somewhat surprisingly, even the strong acid and base solutions drifted substantially. Table 4.3 lists the pH values measured at the conclusion of the sequence of experiments.

TABLE 4.3. pH Values at End of Experimental Sampling Sequence

Solution	Initial pH	Final pH		
		40°C	70°C	90°C
HCl	1.03	1.44	2.55	2.20
HCl	2.98	4.16	6.78	8.63
DI Water	5.98	8.41	9.27	9.61
NH ₄ OH	11.30	11.05	10.34	9.99

It appears that pH comes close to the final values within a few days so it is these pH values rather than the initial ones that must be used for interpretation of pH effects on dissolution.

Chemical analysis of the solution samples provided data for plots of concentration against time. To provide a more useful comparison between elements present in the glass at widely different concentrations, all of the concentrations were normalized as a fraction of element released by the formula

$$Nf_i = \frac{C_i [V_s - 0.001 (n-1)]}{1000 W_i} \quad (4.1)$$

where Nf_i = fraction of element i released into solution, C_i = concentration analyzed (mg/L), V_s = volume of solution at beginning of experiment (0.1 L in all experiments), n = sequential number of sampling, and W_i = weight of element introduced in initial glass sample.

4.4.2 Results

It was shown in Chapter 1 that boron is a good index element in that its concentration measures the rate of breakdown of the glass-forming framework and it is not removed from solution by saturation and precipitation effects. Figures 4.22 through 4.25 show the release of several elements normalized to boron. The curves are for most part horizontal straight lines within the scatter of the data. This indicates that at low pH the glass is dissolving uniformly with time; there are no new mechanisms appearing at long times. However, the glass is not dissolving congruently since the weight fraction of most elements, including sodium, is less than that of boron. Uranium is extracted at a more rapid rate than boron. Since the same mechanisms seem to be operating, normalizing the release rates to boron also has the effect of normalizing out the temperature dependence of the release rates. The plots of Al, particularly, and some of the other

FIGURE 4.22. Release of Uranium and Matrix Elements Normalized to Boron Concentration; 90°C and pH = 1

FIGURE 4.23. Release of Uranium and Matrix Elements Normalized to Boron Concentrations; 90°C and Initial pH = 3

FIGURE 4.24. Release of Uranium and Matrix Elements Normalized to Boron Concentration; 90°C in Deionized Water

FIGURE 4.25. Release of Uranium and Matrix Elements Normalized to Boron Concentration; 90°C and Initial pH = 11

elements at the intermediate pH values tend to be erratic because of the ratioing of fairly small initial concentration. The release rate of uranium quickly falls below the boron reference line and continues to decrease with increasing pH. In solutions which initially were highly acidic, uranium is continuously extracted in increasing amounts at higher temperatures. In solutions which began at pH = 3 or above the rate of release of uranium is very small.

Figures 4.26-4.28 show the behavior of a few of the other elements in the MCC reference glass under dissolution in a solution with initial pH = 1. Iron is of interest because it reacts readily to form a highly insoluble ferric hydroxide precipitate in all solutions except those of extreme acidity. At 40°C, the drift in pH is small (see Table 4.3). The extraction of iron from the glass continues at a nearly constant rate over the

FIGURE 4.26. Release of Iron and Other Elements at 40°C and pH = 1

FIGURE 4.27. Release of Iron and Other Elements at 70°C and pH = 1

FIGURE 4.28. Release of Iron and Other Elements at 90°C and pH = 1

duration of the experiments. At a temperature of 70°C, the iron concentration reaches a maximum value in about 10 days and then falls off rapidly, presumably with the formation of a ferric hydroxide precipitate. The same phenomenon is observed at 90°C but the fall-off occurs much earlier. These unusual response curves for iron are attributed to the upward drift in pH over the course of the experiments. The pH need only exceed 2 for

the solubility of ferric oxide to drop to very low values.

4.5 ACTINIDE RELEASE

4.5.1 Leach Data - Stable Elements

The leaching tests reported in this section were performed on two simulated nuclear waste glasses; an MCC 76-68 commercial waste glass

and a DWRG. Standard MCC-1 experimental procedures were used in all tests. The results from tests on the MCC 76-68 glass have been previously reported (McVay and Buckwalter 1983).

The DWRG used in these leach rate tests was supplied with uranium doping only. In order to evaluate the release of uranium (other actinides and nonradioactive glass components) and to compare the release behavior of actinides with other actinides, ^{239}Pu and ^{237}Np were doped individually into the reference glass. Bars of previously melted and cast uranium-doped glass were prepared for actinide doping by crushing and sieving to -100 mesh size fraction. The dopant solution was prepared by dissolving PuO_2 or NpO_2 powder in nitric acid solution and diluting this with deionized water to the desired concentration level. The dopant solution was added to the powdered glass, mechanically mixed, and then heated on a hot plate until dry. The doped glass powder was then melted in a platinum crucible at 1100°C for 30 minutes before casting. The glass bars were cast into a steel bar mold assembly preheated on a hot plate. When the bars were sufficiently solidified, they were transferred to an auxiliary furnace where they were held at 500°C for two hours and furnace-cooled to room temperature. The dopant levels, 0.03 wt% PuO_2 and 0.007 wt% NpO_2 , are higher than those anticipated in the real defense waste glass (0.003 wt% PuO_2 and 0.0013 wt% NpO_2) but were necessary for analytical reasons. These dopant levels assure that actinide concentrations measured in solution were not limited by available inventory because of the low waste form surface-area-to-solution-volume used in the tests.

Four leachants were investigated: deionized water, a simulated basalt ground water (Jones 1982), a Permian Basin brine, and tuff ground water obtained from Well J-13 near the Yucca Mountain site. The compositions and initial pH values are listed in Table 4.4.

Examples of the nonradioactive elemental leaching from ^{237}Np -doped MCC reference defense waste glass are given in Figures 4.29, 4.30, and 4.31 for B, Si, and Na, respectively. The experiments were conducted at 90°C with an $\text{SA/V} = 10 \text{ m}^{-1}$. These curves show the effects of tuff and basalt ground water compared to deionized water and the interactive effect of iron. The data plotted is direct unfiltered elemental concentration in solution, which includes the truly soluble species as well as any colloids that may be in solution.

TABLE 4.4. Ground Water Compositions Used in Tests on DWRG

Constituent	Amount Present (mg/L)		
	Tuff Water	Basalt Water	Salt Brine
Ca	13.2	1.3	1,560
K	5.0	1.9	39
Mg	2.1	0.04	134
Na	47.0	263.0	123,000
Sr	0.004	--	35
Si	30.2	56.0	--
Zn	--	--	7.8
F^-	2.1	37.0	1.1
Cl^-	7.4	148.0	191,000
CO_3^{2-}	0.0	27.0	0.0
HCO_3^-	120.0	70.0	30
SO_4^{2-}	18.3	109.0	3,200
NO_3^-	8.0	1.3	--
pH	7.5-8.5	9.0-10.0	6.7-7.7

There is a general tendency for elemental leaching to be depressed with increasing silicon content of the ground water. The fact that dissolved silicon solution concentration is important in modifying glass dissolution rates has been demonstrated for MCC 76-68 glass (McVay and Buckwalter 1983). Samples of that glass have been leached in silicic acid solutions of varying concentrations and in two actual ground waters that contained dissolved silicon. Boron was measured in the leach solution because it is a major network-forming component of the glass not originally present in the solutions, yet it does not readily form secondary alteration products or precipitates. Thus, boron is an index of glass dissolution rate. Boron solution concentrations, normalized by the elemental proportion in the solid and the sample surface area, measured from 28-day leach tests on MCC 76-68 glass are plotted versus initial silicon concentrations in Figure 4.32. Dissolution of boron (as well as many other soluble glass components) shows an approximate inverse relationship to the initial amount of dissolved silicon in both silicic acid solutions and in the more complex ground waters. A qualitatively similar relationship is observed for boron (Figure 4.29) and sodium (Figure 4.31) release from the DWRG.

This behavior is readily understood by a reaction model in which the overall rate of

FIGURE 4.29. Boron Release from Neptunium-237 Doped MCC DWRG Versus Test Duration. Tests performed at 90°C with SA/V = 10 m⁻¹.

FIGURE 4.30. Silicon Release from Neptunium-237 Doped MCC DWRG Versus Test Duration. Tests Performed at 90°C with SA/V = 10 m⁻¹.

FIGURE 4.31. Sodium Release from Neptunium-237 Doped MCC DWRG Versus Test Duration. Tests performed at 90°C with SA/V = 10 m⁻¹.

FIGURE 4.32. Boron Release Following 28 Days of Leaching of Borosilicate Glass at 90°C Versus the Initial Silicon Concentration. Dissolution of all soluble components was sharply reduced by dissolved silicon.

dissolution is controlled by the rate-limiting step of dissolution of the least soluble major component, SiO_2 in this case. From basic kinetic rate theory on dissolution, the rate of dissolution of the rate-limiting component can, in turn, be directly related to the degree of undersaturation (as a measure of the difference in chemical potential) in the coexisting solution (Berner 1978; Lasaga 1981). The higher the initial SiO_2 solution concentration, the lower the degree of undersaturation; i.e., the lower the chemical potential difference driving dissolution and, thus, the slower the dissolution of SiO_2 as well as other more soluble components. We must caution, however, that such a simple model assumes a single dissolving/reacting solid phase, (a) congruent dissolution, no precipitation of

secondary phases, and no complexation reactions in solutions that may change effective chemical concentrations. Clearly, some or all of these assumptions will probably be violated under actual repository conditions.

The addition of ductile iron as a metallic barrier component can result in totally different leaching behavior (Figures 4.33-4.35). This is not unexpected because the introduction of a highly reactive (metallic iron lies below the lower redox stability limit of water at all pH values) second solid of different composition must necessarily lead to additional interactive or synergistic effects. These include a separate reaction between the iron and the aqueous solution, as well as a reaction of iron with the waste form conducted by mass transfer through the solution.

(a) Note that at saturation, the dissolution rate of a solid phase does not equal zero. A solubility limit implies a balancing of forward (dissolution) and back (precipitation) reaction rates of the identical phase resulting in no net change in solution concentration. Steady-state reaction is similar, except that it is a nonequilibrium condition in which the dissolving phase and the precipitating phase are not necessarily identical (Lasaga 1981).

Placing ductile iron in aerated (i.e., initially oxidic) basalt or tuff ground water, without glass present, tends to remove many of the elements and make the two ground waters somewhat more similar in composition, as shown in Figures 33 and 34 for Si and Ca from McVay and Buckwalter (1983). Figure 4.33 shows the time dependence for removal of silicon from both basalt and tuff ground waters by ductile iron at 90°C with an SA/V ratio of 10 m^{-1} . The results show a rapid removal of

FIGURE 4.33. Time-Dependent Changes in Si Concentrations of 90°C Basalt and Tuff Ground Waters When Exposed to Ductile Iron at SA/V Ratio of 10 m^{-1}

FIGURE 4.34. Time-Dependent Changes in Ca Concentrations of 90°C Basalt and Tuff Ground Waters When Exposed to Ductile Iron at SA/V Ratio of 10 m^{-1}

silicon from both ground waters by the iron. The total amount of silicon in solution, including colloids, is shown by the dashed lines. After filtration of the leachate through 200- μm filters, the amount of silicon in solution decreased, due to removal of the colloids, as shown by the solid lines. Further filtration through 100- and 1.8- μm filters removed no additional silicon. Basalt and tuff ground waters have initial silicon concentrations of 56 and 30 ppm, respectively. Yet, after a short exposure to iron, the silicon concentrations are equal. Most of the silicon forms a precipitate on the surface of the iron coupon. Colloids are also formed, however, as can be seen from Figure 4.33. Similar results are found for calcium removal from basalt and tuff ground waters by iron (Figure 4.34).

In leach tests on both MCC 76-68 commercial waste glass (McVay and Buckwalter 1983) and DWRG the presence of ductile iron also causes formation of precipitates, at least part of which are colloidal in nature. Silicon is rapidly removed from both basalt and tuff ground waters, as shown in Figure 4.30. The precipitates are essentially X-ray amorphous. Analyses by EDAX and XRF of the

filtered precipitates show them to contain primarily iron and silicon (possibly amorphous greenalite, $3\text{FeO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) with many other elements present in trace quantities.^(a) Furthermore, the surfaces of the iron coupon present during leaching are discontinuously covered by large quantities of loosely adherent iron silicate precipitates. Precipitates of similar composition also form to a lesser degree on the glass sample. They are primarily on the "up" side surfaces, indicating that the precipitates form directly from solution rather than by strong surface interactions between glass/iron and solution.

(a) At this time it cannot be ruled out that the precipitates are mixtures of iron oxides ($\text{Fe}(\text{OH})_3$) and silica (SiO_2), perhaps including some actual iron silicate also. Jantzen (1984) has performed a similar test on a SRL-165 reference defense waste glass plus ductile iron in a reference basalt ground water and found poorly crystallized precipitates of both greenalite and iron hydroxide.

FIGURE 4.35. Illustration of Two Effects on Leaching Characteristics of PNL 76-68 Glass, i.e., Effect of Ground Water Composition Without Iron Present and Effect of Having Iron Present During Leaching

It was previously stated that tuff and basalt ground waters caused less elemental removal from glass samples than deionized water because their starting compositions contain many elements normally leached from the glass. Leach rates tend to decrease as the elemental concentrations increase in solution. As can be seen from Figures 4.33 and 4.34, however, the presence of iron causes the ground water compositions to lose many of their elements and to approach deionized water in effective composition. Therefore, when ductile iron is placed in the leachates along with glass, the effect of ground water composition on leaching is greatly reduced and it is expected that all three (deionized, basalt, tuff) ground water solutions will lead to similar leaching behavior. This is confirmed for MCC 76-68 glass in Figures 4.35 and 4.36 and for DWRG in Figures 4.29 and 4.31. Furthermore, the presence of metallic

iron enhances the overall leaching of both glasses relative to even the leaching in deionized water in the absence of metallic iron (Figures 4.29, 4.31, and 4.35). This effect is particularly evident for B and Na, which do not readily form alteration products or precipitates and are, therefore, prime indicators of the degree of glass reaction.

The apparent mechanism for this enhanced attack is that metallic iron undergoes corrosive oxidation in the presence of water, releasing ferrous ions. These ferrous ions scavenge dissolved silica from solution, forming a stable ferrous-iron silicate precipitate. Precipitation, in turn, causes the leachant to become undersaturated with respect to silica (Figure 4.30), driving further dissolution of the glass. This model is supported by the much larger depletion-layer

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FIGURE 4.36. Scanning Electron Micrographs of Cross Sections of PNL 76-68 Glass, i.e., Effect of Ground Water Composition Without Iron Present and Effect of Having Iron Present During Leaching

depths for glasses observed from tests with metallic iron (Figure 4.36). Jantzen (1984) has proposed a similar mechanistic model from independent tests on a reference SRL defense glass plus ductile iron in a reference basalt ground water.

4.5.2 Leach Data - Actinide Elements

4.5.2.1 Neptunium-237

The release of ^{237}Np from DWRG is illustrated in Figures 4.37 through 4.39 for deionized water, reference basalt ground water, and salt brine held at 90°C at an initial SA/V of 10 m^{-1} .

The effect of iron on ^{237}Np release is also shown. The iron surface area was initially equal to that of the glass. The actinide concentrations plotted on Figures 4.37 through 4.39 include the direct measurement of concentration from unfiltered solution, the concentration of solution filtered through a $1.8\text{ }\mu\text{m}$ filter (i.e., the truly dissolved as soluble fraction), the concentration of solution from an acid stripping of the post-experiment reaction vessel surfaces, and the concentration of solution from an acid stripping of the post-experiment iron coupon. Note that the latter two concentrations are presented as the mass of a given actinide removed, normalized to the actual volume of solution used in the experiment.

FIGURE 4.37a. Neptunium-237 Release in Deionized Water Solution (90°C)

FIGURE 4.37b. Neptunium-237 Release in Deionized Water Solution with Iron (90°C)

FIGURE 38a. Neptunium-237 Release in Brine Solution (90°C)

FIGURE 4.38b. Neptunium-237 Release in Brine Solution with Iron (90°C)

FIGURE 4.39a. Neptunium-237 Release in Basalt Solution (90°C)

FIGURE 4.39b. Neptunium-237 Release in Basalt Solution with Iron (90°C)

Therefore, all these individual concentrations^(a) can be added together to give a total concentration of actinide released from the glass. This total concentration is also shown in the figures.

Leach test data on ^{237}Np release in deionized water tests are plotted on Figures 4.37a and 4.37b. For deionized water alone, only a small portion of the total ^{237}Np in solution is truly dissolved (10 to 20%), while the remainder occurs as a colloidal fraction greater than 1.8 nm in diameter (Figure 4.37a). The addition of iron results in a much higher amount of colloidal ^{237}Np initially introduced into solution, although the truly dissolved or soluble concentration is about the same as the deionized water-alone test. The major effect is the large amount of ^{237}Np associated with the iron. By 56 days this represents the largest fraction of ^{237}Np removed from the glass. The inverse trends of the direct and iron lines on Figure 4.37b suggest that the ^{237}Np may be transferring to the iron as the result of settling out of colloidal material containing ^{237}Np rather than by increasing sorption of ^{237}Np onto the metal. Longer run times and radio-analytical counting of precipitates on the iron would be necessary to resolve this. Figures 4.37a and 4.37b show that the overall effect of iron on ^{237}Np glass leaching in deionized water is to increase the amount of ^{237}Np released by a factor of 3 or 4 and is attributable to formation of ^{237}Np -bearing precipitates and/or ^{237}Np sorption onto the iron.

Figures 4.38a and 4.38b show the release of ^{237}Np in brine solution as a function of time. Although there is some scatter, Figure 4.38a shows that the direct and filtered concentrations are nearly identical, indicating that the major function of ^{237}Np in brine solution is as a soluble rather than colloidal form. When iron is added (Figure 4.38b), both absolute concentration and fractional proportion of soluble ^{237}Np in solution decreases. There is also a simultaneous increase in both the absolute amount and fractional proportion of colloidal ^{237}Np , as measured by the direct concentration. A small constant amount of released ^{237}Np is associ-

ated with the iron. The total enhancement of ^{237}Np release by introduction of iron is, however, not great (Figures 4.38a versus 4.38b).

The release behavior of ^{237}Np as a function of time for basalt ground water tests is shown in Figures 4.39a and 4.39b. The majority of ^{237}Np occurs as a soluble form in basalt water-only tests (Figure 4.39a), although there is considerable variation and the colloidal fraction may be approximately equal to the soluble fraction. Addition of iron (Figure 4.39b) results in a large continued increase in the amount of colloidal ^{237}Np in solution while the amount of soluble ^{237}Np is essentially unchanged from the basalt ground water-only test. An appreciable amount (approximately 50%) of ^{237}Np that is released is associated with the iron. Figures 4.39a and 4.39b show that the presence of iron causes the total release of ^{237}Np to increase substantially as a function of time for glass leaching in basalt ground water.

Table 4.5 summarizes the total amount of ^{237}Np released from the glass and the percent of released ^{237}Np associated with colloidal material, true solution (i.e., filtered solution), the iron coupon if present, and the acid strip of the fraction vessel walls. The percentage data are particularly effective in showing the relative impacts of the addition of iron in each of the three solution systems.

In general, the total amount of ^{237}Np removed from the glass is larger if iron is present, but the effect is less in brine than in the other solutions tested. This was also observed for tests performed with MCC 75-68 glass (McVay and Buckwalter 1983). Also, when iron is present, almost all of the ^{237}Np is removed by filtration through a 1.8 nm filter (Figures 4.37b, 4.38b, and 4.39b; Table 4.5). That is, the ^{237}Np in solution does not occur dominantly as a soluble species but is associated with the colloidal fraction. The ^{237}Np released by the glass ends up primarily on filterable colloids and the surface of the iron. Thus, depending on the fate of the colloids, the effect of iron could be beneficial in controlling the release of radionuclides from the waste package. There is also a general tendency for the amount of soluble ^{237}Np to decrease when iron is present. This may be attributable to the fact that the corrosion of iron in aqueous solution will impose a localized reducing environment (Jantzen 1984). Reducing conditions typically lower the solubilities of actinide-containing solids (Grambow 1982; Early et al. 1982; Jensen 1982; Rai and Ryan

(a) Excluding the concentration for the filtered solution that represents the truly soluble fraction within the direct concentration measurement. Note that the differences between the direct and filtered concentrations is the concentration of the filterable, colloidal portion of the actinide in solution.

TABLE 4.5. Systematics of ^{237}Np Release After 56-Day Duration^(a)

System	Total Release (ppb)	Colloidal	Filtered	Iron	Acid Strip
Brine	2.6 ± 0.5	5%	65%	-	30%
Brine + Iron	4.3 ± 0.5	60%	10%	20%	10%
Basalt Water	3.0 ± 0.3	30%	50%	-	20%
Basalt Water + Iron	27.0 ± 1.0	40%	< 1%	50%	10%
D.I. Water	6.0 ± 0.5	← 90% →		-	10%
D.I. Water + Iron	19.0 ± 1.0	20%	5%	70%	5%

(a) Leach tests at 90°C.

1984) as well as other radionuclide-bearing solids (Schreiber et al. 1982b; 1983a).

4.5.2.2 Plutonium-239

The release of ^{239}Pu from MCC reference defense waste glass is shown in Figures 4.40, 4.41, and 4.42 for deionized water, reference basalt ground water, and salt brine—with and without the presence of iron. The test conditions and parameters were identical to those for the ^{237}Np doped glass (see Section 4.5). The designations of the specific lines showing concentration versus time have been discussed in the previous section.

For leaching in distilled water (Figure 4.40a), ^{239}Pu occurs in solution dominantly as a filterable colloid fraction greater than 1.8 μm in diameter. The absolute concentration of this colloidal ^{239}Pu is increasing with time, while the acid stripped portion of released ^{239}Pu remains approximately constant. The addition of iron (Figure 4.40b) significantly increases the absolute amount of filterable colloidal ^{239}Pu , although there is no change (or even a decrease) in the amount of soluble ^{239}Pu . An appreciable amount of ^{239}Pu is associated with the iron phase relative to the amount acid stripped from the container surfaces. Figures 4.40a and 4.40b indicate that the presence of iron increases the release of ^{239}Pu from the glass by a factor of 10 after 56 days in deionized water, although the total ^{239}Pu released is continuing to increase in both tests.

There is little difference between the direct and filtered ^{239}Pu concentration for leaching in brine alone (Figure 4.41a), signifying that ^{239}Pu is present dominantly as a soluble rather than colloidal species. Figure 4.41b indicates that when iron is present, however, the absolute amount of colloidal ^{239}Pu increases by approximately a factor of 5 while the amount of soluble ^{239}Pu decreases. Unlike the case for deionized water, only a very small amount of ^{239}Pu release from the glass is associated with the iron. The amount of ^{239}Pu attached to the container walls is relatively unaffected by the presence of iron. The total release of ^{239}Pu as a function of time is greater by a factor of 5 when iron is present in brine (see Figures 4.41a and 4.41b).

Figure 4.42a shows appreciable scatter in the basalt-water leaching data because the ^{239}Pu concentrations are significantly lower (approaching the detection limits), in the basalt ground water test than in tests with the other ground waters. For example, compare Figure 4.42a with Figures 4.40a and 4.41a. The soluble ^{239}Pu represents a high proportion, if not the dominant form of ^{239}Pu , in the ground water relative to colloidal ^{239}Pu . When iron is present (Figure 4.42b), the amount of colloidal ^{239}Pu increases substantially. The amount of ^{239}Pu released from the glass as soluble ^{239}Pu remains at or below detection levels, as do the amounts of ^{239}Pu associated with the iron phase and sorbed onto the container surfaces. There is an overall factor of 30 enhancement in ^{239}Pu

FIGURE 4.40a. Plutonium-239 Release in Deionized Water Solution (90°C)

FIGURE 4.40b. Plutonium-239 Release in Deionized Water Solution with Iron (90°C)

FIGURE 4.41a. Plutonium-239 Release in Brine Solution (90°C)

FIGURE 4.41b. Plutonium-239 Release in Brine Solution with Iron (90°C)

FIGURE 4.42a. Plutonium-239 Release in Basalt Solution (90°C)

FIGURE 4.42b Plutonium-239 Release in Basalt Solution with Iron (90°C)

released from the glass when iron is present in the basalt ground water test (Figures 4.42a and 4.42b), attributable almost entirely to the substantial increase in colloidal Pu in solution.

Table 4.6 summarized the total release of ^{239}Pu in each solution system and the relative percentage of that total associated with colloids, true solution (filtered), the iron coupon, and the acid strip of the vessel walls. The conclusions regarding the release of ^{239}Pu from various ground waters, with and without the presence of iron, are similar to those regarding ^{237}Np . In general, the presence of iron accelerates the rate of ^{239}Pu release from the glass. As for ^{237}Np , this effect is less for the brine solution. When iron is present, the dominant form of ^{239}Pu in solution is as filterable, colloidal ^{239}Pu . It is not known whether this colloid fraction represents true ^{239}Pu colloids or pseudo colloids (i.e., ^{239}Pu sorbed onto a precipitate) or a mixture. Depending on the size, charge, mobility, and subsequent interactions of these ^{239}Pu colloids, the interactive effect of iron on the waste glass could be beneficial. There is evidence that the truly soluble portion of ^{239}Pu released from the glass is lower in the presence of iron for all ground waters. This may be related to the local reducing conditions produced by corrosion of iron by water.

4.5.2.3 Uranium

Uranium solution concentrations were measured in addition to ^{239}Pu and ^{237}Np for the same

tests using brine and reference basalt ground water. These data are plotted in Figures 4.43 through 4.46. The designations of the specific lines for concentration versus time have been presented in previous sections.

In leach tests with brine the dominant form of uranium in solution was the truly soluble specie (or species) with very little, if any, colloidal uranium present. The amount of uranium in solution appears to leach a maximum value after 10 days and then decreases to a steady value after 28 days. This decrease may be associated with formation of a uranium-bearing precipitate or sorption onto the container walls. The total uranium release did increase with time, reflecting a steady increase in the amount of uranium sorbed onto the walls of the container. Comparison of Figures 4.43a and 4.43b shows that the uranium release in brine solution was essentially the same for either the Pu-doped or Np-doped glass with the absolute uranium concentrations being perhaps slightly higher in the case of Pu-doped glass. Comparisons of Figures 4.44a and 4.44b of uranium release to brine solution with iron for Pu-doped and Np-doped, respectively, confirms the same similarity in release behavior. Note, however, that in the presence of iron the filterable colloidal uranium fraction increases greatly, while the truly soluble fraction of uranium remains essentially unchanged from tests with brine solution without iron. The amounts of released uranium associated with either the container walls or iron specimen is small relative to the colloidal fraction

TABLE 4.6. Systematics of ^{239}Pu Release After 56-Day Duration^(a)

System	Total Release (ppb)	Colloidal	Filtered	Iron	Acid Strip
Brine	0.43 ± 0.05	10%	65%	-	25%
Brine + Iron	2.05 ± 0.05	80%	< 1%	5%	15%
Basalt Water	0.14 ± 0.03	15%	50%	-	35%
Basalt Water + Iron	4.85 ± 0.15	90%	< 1%	5%	5%
D.I. Water	1.00 ± 0.05	← 60% →		-	40%
D.I. Water + Iron	16.3 ± 1.5	70%	< 1%	5%	25%

(a) Leach tests at 90°C.

FIGURE 4.43a. Uranium Release from Pu-Doped Glass in Brine Solution (90°C)

FIGURE 4.43b. Uranium Released from Np-Doped Glass in Brine Solution (90°C)

FIGURE 4.44a. Uranium Release from Pu-Doped Glass in Brine Solution with Iron (90°C)

FIGURE 4.44b. Uranium Release from Np-Doped Glass in Brine Solution with Iron (90°C)

FIGURE 4.45a. Uranium Release from Pu-Doped Glass in Basalt Solution (90°C)

FIGURE 4.45b. Uranium Release from Np-Doped Glass in Basalt Solution (90°C)

FIGURE 4.46a. Uranium Release from Pu-Doped Glass in Basalt Solution with Iron (90°C)

FIGURE 4.46b. Uranium Release from Np-Doped Glass in Basalt Solution with Iron (90°C)

and remains constant over time for both. The total amount of uranium released from the glass continued to increase up to at least 56 days, reflecting the fact that colloidal uranium was continuing to increase up to this time.

Figures 4.45a and 4.45b show the release behavior of uranium from Pu-doped and Np-doped glasses, respectively, in basalt ground water. Essentially all of the uranium released is as truly soluble species, with negligible amounts of filterable colloidal uranium or uranium sorbed onto container walls. This is similar to the brine solution test results, but the total amount of uranium released after 56 days is higher by a factor of ten for the basalt ground water than for similar brine solution tests. Within analytical uncertainties, the data for uranium release from a Pu-doped glass are identical to the data for uranium release from a Np-doped glass for the basalt ground water tests. Uranium also shows a qualitatively similar behavior for release from both glasses when tested in basalt ground water plus iron, as indicated by Figures 4.46a and 4.46b. The presence of iron significantly decreases the amount of soluble uranium in solution, perhaps as the result of localized reduction of soluble U^{6+} to insoluble U^{4+} at the surface of the iron specimen. The amount of filterable colloidal uranium is greatly increased by the presence of iron, and this form of uranium dominates the total uranium in solution.

The amount of uranium associated with the iron specimen is also large, as might be expected if insoluble U^{4+} compounds were forming at its surface. But, interestingly, the amount of uranium associated with the iron in basalt ground water is large only for

short duration (<28 day) tests. In fact, the direct solution concentration (mostly of filterable colloidal uranium) shows an inverse relationship to uranium associated with the iron. As the former increases after 28 days, the latter decreases. This may indicate that the colloidal uranium in solution is material that actually formed at the surface of the iron specimen and is gradually being released by continued corrosion of the iron. Alternatively, the inverse relationship may arise from a gradual but continuous decrease in the redox potential (Eh) of basalt ground water in the presence of iron (Jantzen 1984; Jacobs and Apted 1981; Apted and Myers 1982; Lane et al. 1984) that could result in a change in the type or rate of competing reactions for the uptake of uranium. Detailed chemical analysis of filterable material and of the iron surface may be required to resolve the overall fate of uranium in this system.

Table 4.7 summarizes the total amount of uranium released in all three solution systems as well as the relative percentages of the total uranium associated with colloidal material, true solution (filtered), the iron coupon, and the acid strip of the vessel walls. Overall, the total release of uranium seems to be decreasing after 56 days, attributable to the greatly decreasing amount of uranium associated with the iron. This trend is somewhat misleading, however, because the concentration of uranium in solution, mostly as a filterable colloidal form, is continuing to increase up to at least 56 days. If the indicated relationship holds, it may be that the direct concentration of uranium will become constant as the amount of uranium associated with the iron specimen approaches zero.

TABLE 4.7. Systems of Uranium Release After 56-Day Duration^(a)

System	Total Release (ppb)	Colloidal	Filtered	Iron	Acid Strip
Brine	0.56 ± 0.10	<1%	5%	-	95%
Brine + Iron	2.17 ± 0.12	80%	<1%	10%	10%
Basalt Water	1.10 ± 0.15	<1%	100%	-	<1%
Basalt Water + Iron	2.86 ± 0.15	75%	5%	15%	5%

(a) Leach tests at 90°C.

The concentration of uranium increases in the reaction layer of DWRG upon leaching as illustrated in Figure 4.47. This is a Rutherford backscattering spectra (RBS) analysis of leached glass reaction layers. The shape of curves indicates that uranium is uniformly enhanced and distributed through the reaction layer. It is not possible to analyze for Pu and Np when uranium is also present in a larger quantity, due to the similarity of their mass. If they are distributed as uranium, one would expect enhanced alpha radiolysis at the surface of the glass due to enriched concentrations of alpha emitters. However, when iron is present, the spectra look quite different as illustrated in Figure 4.48. In this case, so much iron covers the surface that nothing else can be seen. It is likely that alpha radiolysis effects from the glass surface will be diminished as a result of the iron covering.

In a Pu-doped MCC 76-68 glass without uranium in the composition, a better RBS analysis of Pu has been made due to lack of uranium interference. These results are indicated in Figure 4.49 and show that, in deionized wa-

ter, Pu surface concentrations increase initially and then decrease as other elements deposit on the surface. In brine, however, the surface is immediately covered and very little Pu is exposed. Comparing these results to the rare-earth actinide simulators, Figure 4.50 shows that a difference (at least in the short term) exists for brine. The rare earths are not distributed in the reaction layer in the same manner as the actinides.

4.5.2.4 Comparison of Actinide Leaching Behavior

Because of safety and radiation hazards associated with use of ^{237}Np , ^{239}Pu , and other actinides, uranium is often considered and used as a less hazardous analogue for actinides in nuclear waste form testing (Clark and Hensch 1982; Stone 1981). Tables 4.5 to 4.7 compile all of the final 56-day concentration data for ^{237}Np , ^{239}Pu and uranium from tests with deionized water, brine solution, and reference basalt ground water--both with and without iron present. Although the results for ^{239}Pu and ^{237}Np are from tests

FIGURE 4.47. Rutherford Backscattering Spectra of MCC Leaching Mechanisms Standard Defense Glass Leached in Deionized Water at 90°C

FIGURE 4.48. Rutherford Backscattering Spectra of DWRG Leached in Deionized Water and Deionized Water Plus Iron at 90°C

FIGURE 4.49. Surface Concentration of Pu in Pu-Doped 76-68 Glass - RBS Analysis

FIGURE 4.50. Surface Concentrations of Nd+Ce+La+Pu in Pu-Doped 76-68 Glass - RBS Analysis

using different dopants in otherwise-identical glasses at identical test conditions, it has been demonstrated that uranium, a component common to the two glasses, showed essentially the same release behavior from both glasses. This supports the validity of combining and comparing the data for all three actinides from the different tests.

For the brine solution plus iron data (Figures 4.38b, 4.41b, 4.44a and 4.44b), all three actinides show an increase in direct solution concentration with time. Uranium is similar to ^{239}Pu in that most of the direct actinide concentration in solution occurs as a filterable colloidal fraction (Tables 4.6 and 4.7). That is, the actinide concentration of the filtered solution contributes negligibly (<1%) to the total direct solution concentration for these actinides. The filtered solution concentration for ^{237}Np , although less than the ^{237}Np concentration occurring as a filterable colloid, does represent 10 to 20 percent of the total ^{237}Np in solution. With respect to interaction with iron, however, uranium is similar in behavior to ^{237}Np rather than ^{239}Pu (Tables 4.5 and 4.6). Note that for both uranium and ^{237}Np in these tests, the amount of actinide associated with the iron specimen represents a significant fraction (>10%) of the total ac-

tinide released from the glass. Apparently, the release behavior of uranium does not fully simulate the release behavior of either ^{237}Np or ^{239}Pu from glass in brine solution with iron present. Obtaining a clear analogy in release behavior among these actinides is further complicated by the fact that reactions are obviously continuing in these systems, and even tentative conclusions about the correlations in chemical behavior should be based on steady-state reaction conditions.

There is also some ambiguity regarding the correlation of uranium release to the release behavior of actinides in leach tests with basalt ground water plus iron (Figures 4.39b, 4.42b, 4.46a, 4.46b). Uranium, ^{239}Pu , and ^{237}Np all occur dominantly in solution as a filterable colloidal fraction rather than as truly soluble species; this tendency is particularly evident for ^{239}Pu (Tables 4.6 through 4.7). Both uranium and ^{237}Np show strong interaction and association with the iron specimen, whereas the amount of ^{239}Pu associated with iron is relatively insignificant, essentially at the same low concentration level as the soluble fraction of ^{239}Pu in solution. The same correlation between uranium and ^{237}Np was indicated from tests in the brine solution with iron. The uranium portion associated with iron shows a marked

decrease with time, however, while the ^{237}Np associated with iron appears to reach a constant maximum value after 28 days. This behavior illustrates the danger of drawing general conclusions regarding similarity in chemical behavior on the basis of systems far from equilibrium. Furthermore, empirical correlation of chemical similarity based on measured solution concentration may be fortuitous and should be confirmed by actinide analysis of associated solids, including filtered colloids and associated barriers such as the iron specimen or host rock material if present.

4.5.3 Solubility Limits to Radionuclide Release

Previous testing of glass waste forms have emphasized the collection of short-term, time-dependent leach rate data (McVay and Buckwalter 1983; Clark and Hench 1981; Stone 1981; Wallace and Wicks 1983). It has been recognized (Grambow 1982; Apted 1982; Rai and Ryan 1984; Wood 1980; Savage and Robbins 1982), however, that time-dependent solubility concentrations, imposed by the formation of alteration products of glass, represent a demonstrable limit to the release of radionuclides over the long time period ($>10,000$ years) during which nuclear waste is potentially hazardous. Solubility limits to radionuclide release are especially relevant for the slow flow of ground water expected in several proposed repositories (Berner 1978; Chambre, Pigford and Zavosky 1982). In the following section, steady-state concentrations of radionuclides obtained in tests of DWRG are compared with solubility concentrations of known radionuclide-bearing solids. In many cases, the close agreement between these concentration values suggests that steady-state concentrations of radionuclides observed in glass waste-form tests are attributable to formation of solubility-limiting solids.

There are several cautionary aspects regarding the assumption that steady-state radionuclide concentration observed in long-term tests on glass waste forms will correspond directly to measured solubilities of radionuclide-bearing solids (Rai and Ryan 1984; Wood 1980; Chambre, Pigford and Zavosky 1982). The first is that the actual radionuclide-bearing solids that form upon alteration of glass may be, and typically are, chemically complex, hydrated, amorphous compounds rather than simple oxide or hydroxide compounds used in solubility studies. This point emphasizes the need for careful analyses of alteration solids at the termination of glass/ground water tests (see Chapter 2).

A second limitation is that the steady-state concentrations observed in glass/ground water tests are commonly achieved by a dynamic balancing of the kinetics of dissolution and precipitation of different solids, rather than by true thermodynamic solubilities (Apted 1982; Savage and Robbins 1982). Lastly, the conditions under which most existing solubility data on radionuclide-bearing compounds have been obtained are distinctly different from the environmental conditions of proposed nuclear waste repositories. Temperature, ionic strength of the ground water, and concentration of complexing anions in natural ground water are three immediate examples of environmental parameters that are different in repository-related glass/ground water tests than in typical, 25°C solubility tests performed in deionized water. Taken together, these problems complicate any attempt to reliably use radionuclide solubility data to predict actual steady-state concentrations of radionuclides released from glass waste forms. Pursuit of solubility data on chemically simple, radionuclide compounds supports, but does not supplant, direct tests on glass waste forms.

4.5.3.1 Plutonium

Figure 4.51 presents 25°C solubility data on amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ (Rai and Ryan 1984) with 56-day Pu-concentration in 48 nm filtered deionized water taken from 40°C and 90°C leach tests performed under air-saturated conditions on DWRG. These 56-day concentrations appear to approach steady-state values; that is, to be unchanging with respect to time. The pH values reported for the 40°C and 90°C data are the pH values measured at 25°C . The Pu concentrations measured from the glass tests are in excellent agreement with values expected if $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ were controlling the concentration. The actual presence of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in the glass tests has not been established, however.

Concentrations of Pu obtained after 56-day, 90°C leach tests on DWRG in brine and basalt ground water are also shown in Figure 4.51. These are 1.8 μm filtered solutions from these tests, representing the truly dissolved amount of Pu released from the glass (Table 4.6). The Pu concentrations for brine and basalt ground water are even lower than those for deionized water. This may be attributable to the different pH's of these solutions and the dependence of solubility and activity of solution species on ionic strength (Early et al. 1982; Rai and Ryan 1984), especially for the concentrated brine solution. The Pu

FIGURE 4.51. Measured Solubility Concentration of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ Compared with Results of 90° Tests on DWRG

concentration for the brine falls considerably below the water solubility concentration. Part of this may be due to the effect of ionic strength on pH in brine. Unpublished work by PNL suggests that values for brines, when corrected for ionic strength, should be displaced at least one pH unit higher (more alkaline).

It is also notable that the 56-day concentrations of Pu in deionized water, brine, and basalt ground water decrease when iron is added (Figure 4.51 and Table 4.6). This may be the result of a decrease in solubility of a plutonium-bearing solid because of lower redox potential in solution (McVay and Buckwalter 1983; Jantzen 1984); or it may be due to the formation of a different, more stable (i.e., less soluble) plutonium-bearing solid when iron is present. In all solutions except basalt ground water, the effect is not large.

4.5.3.2 Neptunium

Measured apparent solubilities of $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ at 25°C in different redox agents are presented in Figure 4.52, along with solid lines showing the solubility of $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ calculated from thermodynamic data (Rai, Ryan and

McCulloch 1984). Also included in Figure 4.52 are data for the apparent steady-state concentrations of Np obtained after 56-day 90°C leach tests on DWRG using deionized water, basalt ground water, and brine (Table 4.5). Concentrations for the leach tests were measured from 1.8 μm filtered solutions. The Np concentrations from the leach tests are lower than the expected Np concentrations based on thermodynamic data, especially at high pH (>7). The leach test concentrations do, however, closely match the solubility of $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ measured using a variety of redox agents (Rai, Ryan and McCulloch 1984).

This correspondence in values is somewhat surprising because of the air-saturated conditions of the leach tests and the reducing conditions of the solubility tests. There are several possible explanations. The first is that the Np concentration in the glass leach test is controlled by the oxidation state of the Np in the glass, which may be in a Np(IV) rather than Np(V) state. When released from the glass by dissolution, the Np (IV) may precipitate more rapidly than it can be oxidized in solution. A second reason may be that the solubility of neptunium-bearing solid is not a strong function of

FIGURE 4.52. Measured Solubility Concentrations of $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ Compared with Results of 90°C Tests in DWRG

redox potential (Early et al. 1982). Another possible reason is that the measured Np concentration in the 56-day test is not yet a steady-state value and is still slowly changing with time.

Figure 4.52 also presents 56-day Np concentration for leach tests using the same ground water solutions with the addition of iron. These concentrations are in excellent agreement with the solubility of $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ measured under reducing conditions. This is consistent with the idea that the addition of iron in leach tests may cause local decreases in redox potential of the solution. Note that, as with Pu, the measured concentration of Np in 56-day leach tests decreases when iron is added to all ground water solutions.

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CHAPTER 5
RADIATION EFFECTS

CHAPTER 5

Radiation Effects

ASSIGNMENT: INVESTIGATE THE EFFECTS OF RADIATION ON LEACHING MECHANISMS

SUMMARY: The principal radiation effects of concern are: a) radiation-induced changes in the waste glass, b) radiolysis at the glass: water interface, and c) radiation-induced changes in the repository environment, including effects on the host rock that may alter water chemistry. Measurable density change in waste glass begins at a cumulative dose of about 1×10^{23} alpha decays/ m^3 and saturation at a dose of approximately 5×10^{24} alpha decays/ m^3 . Leach rates increase by less than a factor of three even in waste glass with a saturated radiation dose. Radiolysis of repository fluids can yield a complex spectrum of products, including, in addition to the normal radiolytic products of water, oxalic and nitric acids from radiolysis of CO_2 and dissolved N_2 , oxidizing chlorine species from radiolysis of Cl^- , and high molecular weight organic compounds from radiolysis of methane. These effects may be mitigated by the presence of host rock and engineered barrier materials, as well as additional redox-sensitive, dissolved species. Tests designed to isolate the effects of the radiolytic products of water on the leaching of plutonium from defense waste glass were performed as part of the Leaching Mechanisms Program. The radiolytic products enhanced the leach rate by about a factor of two.

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CHAPTER 5.0

RADIATION EFFECTS

5.1 INTRODUCTION

Waste form leaching studies have typically been conducted with chemically simple, aqueous solutions in the absence of both radiation fields and other waste-package barrier materials. This approach has led to an understanding of waste form behavior under an idealized environment that may have limited application to actual repository conditions. Because reliable long-term prediction of radionuclide release characteristics from a waste package and repository is required for licensing (Nuclear Regulatory Commission 1982), it is necessary to understand the effects of radiation on radionuclide release from waste forms, both alone and in the presence of appropriate barrier materials.

The information reported in this chapter focuses on three broad areas of radiation effects. These are:

- waste form radiation damage
- radiolysis of ground water solutions
- host rock radiation damage.

The sections on radiation damage of waste forms and repository host rock (salt in particular) review the current literature on these effects. The section on radiolysis presents and summarizes the bulk of new experimental data generated for this program.

New experiments on radiolysis effects for this program have been restricted to alpha radiolysis in a variety of ground waters because of time and funding limitations. In order to evaluate the interactive effects of barrier materials, alpha radiolysis tests have been conducted on the following systems:

- ground water
- ground water + borosilicate glass.

The main emphasis in testing in the Leaching Mechanisms Program has been on actinide-doped MCC reference defense waste glass (DWRG). Some results of these tests were reported in Chapter 4; the remainder in Section 5.3.4.3.

5.2 WASTE FORM RADIATION DAMAGE

5.2.1 Summary

Data on the effects of beta and gamma radiation on structural damage to nuclear waste forms, and subsequent leaching performance of such irradiated waste forms, are meager. Based on analogy to simpler oxide and silicate materials, these types of radiations are not expected to contribute significantly to structural disordering (amorphization) of the solid. With respect to alpha irradiation, ceramic and glass nuclear waste forms display qualitatively similar behavior (i.e., changes in bulk volume, threshold, and saturation effects), related to increasing structural damage/disordering. Measurable structural damage begins at a cumulative dose of about 1×10^{23} alpha decays/m³ and "saturates" at a dose of approximately 5×10^{24} alpha decays/m³. These doses correspond to cumulative doses expected for commercial glasses within the first 10,000 years of disposal in a geologic repository. A rough correlation between degree of structural damage, as measured by percent increase in solid volume, and enhancement of initial leach rate has been established for a wide range of irradiated nuclear waste forms. The solubility of radionuclide-bearing solids has also been demonstrated to be a function of structural disorder due to self-induced alpha radiation damage.

5.2.2 Structural Effects

Nuclear waste forms will be subjected to alpha, beta, and gamma self-irradiation; estimates of the different radiation doses that can be expected have been made previously (Weber and Roberts 1983; Weber 1983; Weber, Turcotte and Roberts 1982; Permar and McDonnell 1981; Burns et al. 1982a). As discussed in these reviews, self-irradiation can induce structural changes that may affect the ability of the waste form to retain radionuclides. In general, the majority of the data available on radiation effects in nuclear waste forms have been obtained by the actinide-doping technique, although other

techniques (external heavy-ion and neutron irradiations) have also been employed to simulate the effects of radiation from alpha decay. The data base on the effects of ionization from beta and gamma radiation produced by fission-product decay are extremely limited. Further, essentially no data are available on the effects of elevated temperatures on radiation-induced changes.

Internal alpha decay and attendant heavy-ion recoil has been demonstrated to cause atomic displacements within a variety of materials, resulting in a disordering (amorphization) of the solid (Weber, Turcotte and Roberts 1982; Burns et al. 1982a; Exarhos 1984). Disorder-induced swelling as a function of dose can be easily monitored by bulk density or X-ray diffraction measurements. Beta, gamma, and external alpha radiation effects are manifested, however, by a different process in which ionization damage results from excitation of bound electrons within localized molecular orbitals. External alpha- and gamma-irradiated materials show only slight swelling relative to alpha recoil effects as a function of dose and exhibit limited tendency toward amorphization (Weber, Turcotte and Roberts 1982; Exarhos 1984).

The dominant radiation damage effects to all nuclear waste forms are expected, therefore, to be related to alpha decay-induced volume changes and attendant amorphization. In glass waste forms, both positive and negative changes have been observed within the range of ± 1 to 2 vol% (Weber and Roberts 1983; Weber 1983). In crystalline ceramic waste forms the volume change is generally positive due to increasing structural disorder. The swelling of ceramics can be substantially higher than in glass, on the order of several percent, because of the higher initial structural ordering of crystalline materials relative to compositionally related glasses. Some individual ceramic phases display swelling of over 10% (Weber and Roberts 1983; Weber, Turcotte and Roberts 1982; Exarhos 1984). More recent results on SYNROC C indicate swelling in excess of 6-7% with associated microcracking (Reeve et al. 1982; Woolfrey, Reeve and Cassidy 1982). Nuclear waste forms usually begin to exhibit swelling changes at a cumulative dose above 1×10^{23} alpha decays/ m^3 (averaged over the entire waste form volume). Saturation of volume changes in both glass and ceramic waste forms is observed at a dose on the order of 5×10^{24} alpha decays/ m^3 . These findings are summarized in Figure 5.1, with cumulative doses contrasted with estimated waste storage times for commercial and defense high-level waste.

5.2.3 Effect on Dissolution of Waste Forms

Data on changes in dissolution of nuclear waste forms due to radiation-induced damage are still scarce. Available leach rate data on actinide-doped waste glasses obtained at or beyond saturation of structural damage indicate that the leach rates increase by less than a factor of three as a result of radiation-induced structural changes from alpha decay (Weber and Roberts 1983; Bibler and Kelley 1978; Burns et al. 1982b, 1982c). There are still insufficient data available to draw conclusions regarding the effects of radiation on leach rates of multiphase crystalline or partially crystalline waste forms. There are, however, data available on related single-phase materials that contribute to the understanding of the potential effects. Most of these studies are concerned with significant structural changes and radiation-induced swelling and amorphization.

Ewing, Haaker and Lutze (1982) have measured increases in leach rates of up to two orders of magnitude as a result of radiation-induced amorphization in natural zircon. Wald and Weber (1984) have reported approximately one order of magnitude increase in leach rates for three relevant Cm-doped materials as a result of amorphization from alpha decay. All of these materials undergo large volume changes as a result of the radiation-induced amorphization, and the observed changes in the short-term leach data may reflect the changes in bonding because of the disordering. Such large changes in dissolution rates as a result of structural disorder are not uncommon. Based on the work of Rimstidt and Barnes (1980), the dissolution rate of fused silica in water at 90°C is a factor of 7.8 times larger than that of crystalline quartz (17% density change) and a factor of 3.1 larger than that of α -cristobalite (5.6% density change). Assuming congruent dissolution, the maximum expected change in leach rate may be empirically related to the change in density, as shown in Figure 5.2, where the solid line represents the upper bound to the existing data. Based on the results in Figures 5.1 and 5.2, the leach rates in waste glasses should not be expected to increase by more than a factor of five due to self-radiation damage (as observed), and the leach rates of crystalline waste forms should increase by no more than a factor of 30.

The effect of radiation-induced changes in macroscopic properties (i.e., bulk density, solid volume, degree of crystallinity by X-ray diffraction) on observed leach rates can perhaps be interpreted on the basis of thermodynamic properties of the waste form

FIGURE 5.1. Expected Volume Changes as a Function of Dose and Correlated to the Waste Storage Times of Both Defense and Commercial High-Level Waste Forms

solid. The rate of dissolution depends upon the chemical potentials driving the dissolution reaction. These chemical potentials are, in turn, related to the free energy of formation of the reacting phases. Amorphization of a solid phase by radiation damage almost certainly will lead to a higher configurational entropy and, thus, a higher free energy of formation for that solid. Within a suite of compositionally related solids, this increase in free energy of formation for a dissolving phase defines a larger overall thermodynamic equilibrium constant for its reaction with water (Rimstidt and Barnes 1980; Dibble and Tiller 1981) and defines a corresponding faster rate of dissolution, as documented by Rimstidt and Barnes (1980) for the simple silica-water system. Thus, the decrease in a parameter such as density, insofar as it can be directly related to an increase in configurational entropy and thus overall free energy of formation, is expected to correlate with enhanced leach rates for solids.

In addition, leach (or dissolution) rates must decrease with time in closed-system conditions because of the effects of solubility limits, back-reactions, and precipitation of new solid phases (see Chapter 6). These effects are coupled with a decrease in the differences in free energy that are driving waste form dissolution (Dibble and Tiller 1981; Aagaard and Helgeson 1982). Therefore, the relative enhancement in leach rates arising from radiation damage, as determined from short-term testing (Figure 5.2), may not accurately reflect long-term radionuclide release behavior of waste forms.

Rai and Ryan (1982) have found, for example, that crystalline PuO_2 gradually converts to a less crystalline PuO_2 form (or a hydrated amorphous compound) with an attendant increase of approximately 100 in the solubility of Pu. However, alpha radioactive decay leads to radiolytic modifications (see Section 5.3) to the coexisting solutions (i.e., local changes in pH and redox potential at the solid surface) as well as structural

FIGURE 5.2. Increase in Relative Leaching L/L_0 Versus Volume Change

disordering of the bulk solid. Such changes in solution composition will independently affect the solubility. It has not been possible to clearly separate radiation damage and radiolysis effects on solubility of radionuclide-bearing solids, although the latter appears to be dominant.

The effects of transmutations on the properties of nuclear waste forms have been under investigation by Gray (1982) at the Pacific Northwest Laboratory. Using ^{134}Cs produced in a reactor, the effects of the Cs to Ba transmutation on density (swelling) and leach rate were studied. Although the study is still ongoing, the results to date show no changes of significance from a waste management viewpoint.

5.3 SOLUTION RADIOLYSIS

5.3.1 Summary

Ground waters exposed to radiation from nuclear waste forms will form free radicals, ionic, and molecular species that can significantly alter the geochemical environment (e.g., pH, redox potential) in repositories. This may result in increased corrosion rates of metallic barriers, enhanced dissolution of waste forms, and complexation of dissolved radionuclides. Gamma radiolysis effects are

key to corrosion studies for the early thermal period of the repository before the gamma-emitting isotopes have decayed. Because of the long half-lives of most alpha emitters, alpha radiolysis effects are of greatest importance to long-term radionuclide release behavior of waste forms. Specific conclusions regarding radiolysis reactions are difficult to formulate because of the many competing radiological, chemical, and physical effects. Reactions between radiolytically produced species and dissolved chemical species (e.g., Cl^- , Fe^{2+} , SO_4^{2-}), the chemical nonreactivity of some radiolysis products, preferential movement of species, presence of dissolved gases, and interactive effects of solids, including waste forms, metallic barriers, and host rocks, all seem to be important factors. In particular, both alpha and gamma radiolysis can generate a more oxidizing environment in repository ground water solutions under certain conditions. This has important implications for the corrosion rate of metals, leaching of waste forms, and enhancement of the solubility limits for radionuclide-bearing phases, including most actinide phases.

5.3.2 General Radiolysis Reactions

The action of ionizing radiation on liquid water is to form reactive radicals and new

molecules by electronic excitation and ionization of the water (Swallow 1973; Allen 1961). The radicals first formed are the hydrated electron, e_{aq}^- (together with an equal number of hydrogen ions, H^+), the hydroxyl and hydroperoxyl radicals, OH and HO_2 , and the hydrogen atom H . The new molecules are hydrogen, H_2 , and hydrogen peroxide, H_2O_2 . The efficiency of the formation or destruction of radiolytic products is expressed by the G value, which is the average number of the product molecules formed or the number of the initial molecules destroyed by the absorption of 100 eV of energy from the radiation. Table 5.1 gives G values for water radiolysis by gamma and 5 MeV alpha radiation. The negative G values for H_2O mean that water is consumed in the reaction. The gamma radiation values apply to tests with gamma radiation and at least approximately to the fission product beta and gamma radiation from the waste glass. The alpha radiation values apply to alpha radiation effects caused by real waste storage glasses and by glasses artificially doped with alpha emitters. An important feature to stress is that G values for radical products are larger than those for molecular products for gamma radiation, whereas the reverse is true for alpha radiation.

These so-called primary radiolytic products can interact with themselves and with other species present in solution to yield secondary products. For example, the gamma radiolysis of pure water produces only a very small equilibrium H_2 concentration because of the rapid reaction between H_2 and radical OH to produce water and radical H . If so-called scavenger ions (such as Cl^-) are present, these may compete with H_2 for the OH radical, thereby raising the concentration of H_2 in solution and increasing its partial pressure in the gas phase. The presence of Cl^- also leads to the secondary products Cl_2^- , ClO^- , ClO_2^- , ClO_3^- , and ClO_4^- . Dissolved carbon dioxide and nitrogen may undergo radiolytic reaction to form oxalic acid and nitric acid, respectively. The presence of potential organic compounds (such as methane) may give rise to the methyl radical. This radical can react with itself and other species within the water to yield a large variety of higher-molecular-weight organic compounds.

The differential chemical reactivity and mobility within solution of radiolytically produced species are also an important consideration in evaluating radiolysis effects. Under alpha radiolysis, for example, equal amounts of reducing and oxidizing species are produced (see Table 5.1). Depending on possible impurities present and temperature effects, however, the primary reducing specie is molecular hydrogen. This specie is chemically inert toward low-temperature aqueous reactions and can become selectively removed from a locally irradiated ground water system because its diffusional mobility is much greater than other species. These factors result in alpha-radiated ground water solutions becoming more oxidizing with time. In so-called silicate ground waters (without solids present), the peroxide formed by alpha radiolysis appears to control the redox potential (Eh) of the solution at oxidizing conditions. Alpha radiolysis of brines, however, results in redox potentials that are higher than those for silicate ground waters, even higher than the thermodynamic stability limit for water as measured by a platinum electrode method (Pederson et al. 1984). This may be caused by the formation of hypochlorite.

Reviews of the role of radiolysis in nuclear waste isolation have been presented elsewhere (Burns et al. 1982a, 1982b, 1982c; Pederson and McVay 1984). Gamma radiolysis effects are most important to metals corrosion and to waste form release in the event of a breach of the waste-package barriers during the thermal pulse period (the first few hundred years). After the thermal pulse period (<300 years), gamma emitters have essentially decayed away, and alpha radiation is too weakly penetrating to cause radiolysis of ground water outside of the waste form canister or container. Radiolysis effects do not become important again until the waste form surface is directly exposed to the ground water. At this time, alpha emitters in the waste form will cause radiolysis of the ground water near the waste form surface. The alpha radiolysis occurs as long as alpha emitters are present, a time scale of millions of years. Therefore, the effects of alpha radiolysis have more impact and more

TABLE 5.1. Primary Radiolytic Species G Values for Gamma and 5 MeV Alpha Radiation

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
5 MeV alpha	0.3	0.3	0.3	0.5	0.10	1.4	1.3	-3.3

importance to long-term waste form release characteristics than gamma radiolysis.

5.3.3 Gamma Radiolysis

5.3.3.1 Salt Brines

In a study on gamma radiolysis of salt brines, the total gas pressure generated by several solutions in a ^{60}Co irradiation field was measured (Gray 1984a). The results for a complex brine, NaCl, and NaBr solutions are shown in Figure 5.3. The gas composition in all cases was about 67% H_2 and 33% O_2 gas, as would be expected (not 75% H_2 and 25% O_2 as previously reported) (Wicks and Ross 1984). It is clear that there is some synergistic interaction between Cl^- and Br^- because the two generate more pressure than the sum of the individual solutions. However, Cl^- and Br^- together still fall short of generating as much pressure as the complex brine.

The effect of Na_2SO_4 is shown in Figure 5.4. By itself, the equilibrium pressure is only about 5 atmospheres. When added to Cl^- , or to Cl^- and Br^- , it appears to be following the brine curve quite well. However, equi-

librium pressures have not yet been determined. Again, the synergism between SO_4^{2-} and Cl^- is quite marked. Based on the preliminary data currently available, it appears that a combination of Cl^- and SO_4^{2-} , and perhaps also Br^- , adequately simulates gas pressures generated by the much more complex brine. The minor constituents in the brine appear not to be important.

Besides H_2 and O_2 , the only other gases found by the mass spectrometer were merely the original air constituents. In particular, no Cl_2 or its derivatives were found in any of the gases analyzed so far. Detection limits for Cl_2 were on the order of 10 ppm. It must be emphasized that high gas pressures can only be realized in a confined space. In particular, the ratio of liquid volume to gas plenum volume must be relatively large.

The results for two complex brine solutions, one containing pieces of iron and the other containing solid salt, are shown in Figure 5.5. The latter was actual salt taken from the bedded deposit. The relative volumes of solution to solid salt were about 4 to 1. The dose normalization procedure was such that one would expect the curve to

FIGURE 5.3. Total Gas Pressures Generated by Salt Solutions in a ^{60}Co Irradiation Field

FIGURE 5.4. The Effect of SO_4^{2-} on the Total Gas Pressures Generated by ^{60}Co Irradiated Field

FIGURE 5.5. Total Gas Pressures Generated by Brine and Solid Waste Package Components in a ^{60}Co Irradiated Field

duplicate the pure brine curve if the solid salt did nothing but occupy space, and that is essentially the case. The brine-containing iron is generating pressure at a slower rate than brine by itself. The reason for this is not yet known.

5.3.3.2 Silicate Ground Water

There are fewer gamma radiolysis studies of so-called silicate ground waters (that is, waters representative of silicate host rock repositories) than there are for salt brines. Silicate waters are generally more dilute than salt brines and can contain larger amounts of a variety of dissolved anions and transition metals that may act as scavenger ions because of their multivalent characteristics. As with salt brines, the use of ground water solutions that are representative of actual repository ground waters is important to achieve maximum relevance for results of radiolysis tests. And, as for salt, the presence of silicate host rock (or waste package barrier materials) coexisting

with ground water undergoing radiolysis may have a mitigating effect on the products of radiolysis.

A study on gamma radiolysis of reference basalt ground water has been conducted (Gray 1984b). Gamma irradiations with a ^{60}Co source were performed on air-saturated and methane-bearing (approximately 700 mg/L) synthetic basalt ground water.

In a 75°C air-saturated test, the gas pressure rose slightly from one atmosphere total pressure to constant value of approximately 2.5 atmospheres total pressure after 26 days of gamma irradiation of 5.7 MRad/hr. An analysis of the final gas composition over the irradiated solution and solution pH is presented in Table 5.2. There was a large amount of H_2 produced and a notable increase in CO_2 . The latter effect may be the result of a much lower pH after irradiation and a consequent decrease in CO_2 solubility in ground water. Surprisingly, there did not appear to be any appreciable change in total

TABLE 5.2. Gamma Radiolysis of Basalt Ground Water With Methane

Solution(a)	BGW	BGW	BGW	BGW	BGW/Fe ^(b)
Irradiation temp. (°C)	65	65	150	150	150
Dose rate (MRad/hr)	1.1	1.1	1.1	5.3	5.3
Total dose (MRad)	340	77	77	380	380
Gas composition (vol%)					
Hydrogen	26	6.1	9.9	24	22
Methane	66	86	85	70	70
Nitrogen	5.4	5.5	5.1	4.2	4.8
Argon	2.9	2.7	0.38 ^(c)	1.8	2.6
Mass 44	0.20	0.40	0.45	0.079	0.16
2,2-dimethylpropane	0.054	0.034	0.52	0.30	0.62
2,2-dimethylbutane	0.022	0.017	0.21	0.075	0.12
Solids analysis					
Mass (g/L)	4.4	2.0	2.4	2.1	2.2
Molecular wt (no av.)	NA ^(d)	630	710	1,040	1,090
Molecular wt (wt av.)	NA	1,550	2,410	2,960	2,930
Carbon (wt%)	-- ^(e)	--	--	86	86
Hydrogen (wt%)	--	--	--	12	12
Oxygen (wt%)	--	--	--	1.0	1.2
Solution pH	9.6	9.6	9.6	9.5	9.3

(a) BGW = basalt groundwater. All solutions were sparged with argon and then equilibrated with 0.14 MPa N_2 and 3.30 MPa CH_4 at 25°C.

(b) This was a duplicate of Test 5 except that iron coupons with a surface area of 20 cm^2 were placed in the liquid whose volume was 60 mL.

(c) The argon concentration was low because of a leak that developed during the initial pressurization with methane.

(d) NA = Not analyzed.

(e) Results did not sum to 100% and therefore are not reported.

N₂ (i.e., no large-scale radiolytic conversion of nitric acid) and O₂ actually significantly decreased. The shift in final pH to a more acidic value may be the result of minor nitric acid generation, although no solution analysis is available to confirm this.

Reference methane- and nitrogen-bearing basalt ground water was gamma irradiated over a range of temperatures (65° and 150°C), radiation dose rate (1.1 and 5.3 MRad/hr), and compositional (with and without the presence of iron) conditions (Gray 1984b). The conditions and post-irradiation analyses for these tests are given in Table 5.3. Total gas pressure increased by no more than 1% during irradiation. Hydrogen was the dominant gas produced, almost exactly at a 1:1 molar ratio with the decrease in CH₄. Nitrogen remained constant or decreased slightly from the irradiation, and no detectable O₂ was produced. A high-molecular-weight organic precipitate was formed that was readily filterable using 0.1 µm filters. The remaining inorganic solution species were present in approximately their initial concentrations. The pH values also remained essentially unchanged. Increasing hydrogen gas concentrations (i.e., increasing degrees of reaction) were correlated with increasing total dose (but not dose rate) and absence of dissolved impurities. An irradiation test on methane-bearing deionized water (see Table 5.3) produced nearly twice the amount of H₂ gas as a similar test on basalt ground water. The presence of iron coupons did not seem to exert any appreciable effect on the radiolysis reactions. Further gamma irradiation tests on this methane-bearing basalt ground water are continuing, using additional barrier materials and increasing the ratio of surface area to solution volume (SA/V) to

TABLE 5.3. Gamma Radiolysis of Basalt Ground Water Without Dissolved Methane. Test conducted at 75°C with a dose rate of 5.7 Mrad/hr for 26 days

	Initial Values	Final Values
N ₂	78%(a)	35%
O ₂	21%	0.6%
CO ₂	0.03%	5.5%
H ₂	--	53.8%
H ₂ O	--	5.1%
Total pressure	1 atm	2.5 atm
pH	9.75	6.5

(a) Gases given in volume percent.

values more relevant to actual repository conditions.

5.3.3.3 Effect on Waste Form Leaching

It has been shown that gamma radiolysis of deionized water accelerates the dissolution rate of borosilicate glass as well as SYNROC by as much as a factor of seven (McVay and Pederson 1981; McVay, Weber and Pederson 1981; Barkatt, Barkatt and Sousanpour 1982, 1983; Nash et al. 1982, 1983; Denatale, Howitt and McElfresh 1982; Solomah 1982). A feature common to all of these studies was that the leachant became acidic due to nitric acid production from radiolysis of air-saturated water. In deaerated water, the accelerated leaching due to radiolysis was smaller than in air-equilibrated water because nitric acid production was eliminated (Pedersen and McVay 1983); the generation of reactive species from water radiolysis is responsible for the remaining enhanced dissolution. The radiolysis effects were also sensitive to gamma-dose rate, showing a marked decrease at less than 10⁵ rad/hr as illustrated in the data of Figure 5.6. The observed increase in leaching in deaerated water ranged from less than a factor of three at 50°C to a negligible contribution at 90°C. The effect of radiolysis was concluded to be temperature independent, however, and the observed changes in leach rate were attributed to the fact that at higher temperatures, other dissolution mechanisms dominate (Pederson and McVay 1983). Similar results have been found in concentrated salt brines (Pederson and McVay 1984).

5.3.4 Alpha Radiolysis

5.3.4.1 Salt Brines

The products of alpha radiolysis of saturated Permian brine are given in Table 5.4 for experiments performed using aqueous ²⁴⁴Cm as an alpha source. The experiments were performed in a glove box with a nitrogen atmosphere. In contrast to gamma radiolysis where H₂/O₂ ratios were 2:1, the ratios were nearly 10:1 following alpha radiolysis. A ratio of exactly 2:1 would indicate a redox potential unchanged by irradiation, essentially as found for gamma radiolysis. The large H₂/O₂ imbalance found after alpha radiolysis would indicate that the brine should become quite oxidizing. It is also apparent that nitric acid may be formed under these conditions. Because essentially all of the energy from alpha decay was absorbed in the solution, the reaction must have occurred in the solution phase.

FIGURE 5.6. Increase in Elemental Leach Rates of MCC 76-68 Waste Glass as a Function of Gamma-Dose Rate at 70°C

TABLE 5.4. Results of Alpha Radiolysis on a Cycle 4 Synthetic Permian Brine Using ^{244}Cm (a)

Days of Equilibration	^{244}Cm (μg)	pH	pe	Gas Composition (%)			
				H_2	H_2O	N_2	O_2
45	174	2.87	21.1	41.4	3.4	47.6	4.5
45	174	2.87	21.1	43.5	3.1	44.7	4.9
43	44	6.08	19.0	15.9	0.9	80.7	2.2
43	44	6.17	18.9	24.7	2.4	69.3	3.1

(a) 48-ml solution, nitrogen atmosphere.

Measurements of solution Eh/pH conditions for several different total alpha doses were made to confirm the implications of the large H_2/O_2 product imbalance, again performed using ^{244}Cm in solution. These results are given in Figure 5.7 and include the expected environmental bounds of ground water systems (Baas Beeking, Kaplan and Moore 1960) as well as expected conditions for a repository in salt, basalt, tuff, and granite in the absence of radiolysis. The effect of alpha radiolysis for total doses of approximately $0.9 - 3.6 \times 10^6$ rad is to raise the redox potential by approximately +1.0 volt over unirradiated brines. Actinide solubilities may be significantly enhanced by the action of alpha radiolysis in concentrated brines.

The fact that alpha radiolysis is so effective at producing oxidizing conditions in brines can be linked to the presence of chlorine. It is necessary to have Cl^- in concentrations approaching 4 M for alpha

radiolysis to rapidly alter Eh. Cations play no detectable role in generation of the oxidizing condition.

5.3.4.2 Silicate Ground Water

There has been very little research conducted on alpha radiolysis of aqueous systems relevant to silicate host rock repositories. Work is now beginning on controlled alpha irradiation of actual reference repository ground waters. This reflects the general limitation in experimental design imposed by the extremely short penetration distances of alpha particles in aqueous solution. It has been noted (Glass 1981) that the largest effect on the yields and steady-state products of radiolysis comes from anions reacting with primary radiolytic species. Sulfate, carbonate/bicarbonate, nitrate, and fluoride as well as chloride are typical anions in silicate ground waters. Unfortunately, relevant alpha radiolysis tests on simple or complex

Ground Water Radiolysis Effects

FIGURE 5.7. Increase in pH Due to Dissolved Irradiated Salt as a Function of Integrated Gamma Dose to the Salt

combinations of these anions at expected concentrations could not be found in the literature. Common major cations, such as sodium, potassium, magnesium, and silicon, are expected to have no direct radiolysis interaction--only an indirect effect caused by an "inert salt effect" that mitigates the rates of reaction between charged species (Glass 1981). Other types of solution species that may affect alpha radiolysis are multivalent transition metals such as iron, copper, uranium, etc. As with gamma radiolysis, the multivalent nature of transition metals can affect alpha radiolysis by a chemical "scavenging" reaction with primary radiolytic species. The effect of dissolved $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{U}^{4+}/\text{U}^{6+}$ on alpha radiolysis of granitic water in contact with spent fuel has been

simulated (Christensen and Bjergbakke, 1982). Over a range of initial values for Fe^{2+} concentration, dissolved gas diffusivities, alpha dose, and rate of Fe^{2+} supply, it was concluded that the presence of dissolved Fe^{2+} can consume radiolytically generated oxygen. Depending on the adjustable parameters, this effect may be able to suppress the increase in solution Eh from autoradiolysis of dissolved actinides (uranium in this case).

5.3.4.3 Effects on Waste Form Leaching

The effect of alpha radiolysis on glass leaching has been evaluated by doping MCC reference defense waste glass with either ^{239}Pu , ^{238}Pu , or combinations of ^{238}Pu and

^{239}Pu . (a) The dopant level was the same for all three glasses and therefore the glass composition was not varied; the only variable was the activity of the glass. The ^{238}Pu has a shorter half-life and is much more radioactive than ^{239}Pu .

This is a realistic test in that the effects of surface damage and water radiolysis are occurring simultaneously. Results for total Pu release from the glass into 40°C deionized water at an SA/V = 10 m⁻¹ are given in Table 5.5. Each experiment was run in triplicate and the results presented are the average. As can be seen, with increased alpha activity, the release of Pu is enhanced by approximately a factor of two. This is true for both 14-day and 56-day exposure times. These results cannot be attributed to pH changes as shown in Table 5.6. Although the pH is becoming slightly more acidic with increased alpha activity, as would be expected from alpha radiolysis, the change is not large enough over the experimental times involved to account for the enhanced Pu release. The pH increases with time are the result of glass reactions with the water. Release of Si from the same experiment is shown in Table 5.7. These results show a slightly increased Si release with alpha activity. Note, however, that the error associated with the analysis of this level of Si is larger than the variation observed.

(a) Additional glass leach tests have also been conducted on ^{237}Np -doped and ^{239}Pu -doped MCC reference defense waste glass and ^{241}Am -doped, ^{237}Np -doped and ^{239}Pu -doped MCC reference 76-68 commercial waste glass. Because these tests did not control or systematically vary alpha activity, these leach results are reported in Chapter 4.

TABLE 5.5. Summary of Total Pu Release in MCC DWRG at 40°C in DI Water

Time, d	Solution	Analysis, ppb		
		P1	P2	P3
14	Leach	1.45	3.16	3.78
	Filtered	1.19	2.84	4.02
	Stripped	1.89	1.57	2.95
56	Leach	4.21	7.82	8.01
	Filtered	3.05	6.45	7.07
	Stripped	0.17	0.16	0.02

P1 = 0.828 wt% Pu-239
P2 = 0.0828 wt% Pu-239
0.07 wt% Pu-238
P3 = 0.86 wt% Pu-238

TABLE 5.6. Summary of pH Change in MCC DWRG at 40°C in DI Water

Sample	Time, d		
	14	28	56
P1	7.35	7.19	7.50
	7.18	7.54	7.37
	7.32	7.37	7.44
	7.28 ± 0.09	7.37 ± 0.18	7.44 ± 0.07
P2	7.25	7.19	7.46
	7.08	7.20	7.28
	7.20	7.25	7.50
	7.18 ± 0.09	7.21 ± 0.03	7.41 ± 0.12
P3	7.09	7.18	7.25
	7.06	7.19	7.23
	7.11	7.18	7.21
	7.09 ± 0.03	7.18 ± 0.01	7.23 ± 0.02

TABLE 5.7. Summary of Si Release in MCC DWRG at 40°C in DI Water

Time, d	Solution	Analysis, ppm		
		P1	P2	P3
14	Leach	0.09	0.09	0.11
	Filtered	0.07	0.07	0.09
	Stripped	--	--	--
28	Leach	0.10	0.13	0.12
	Filtered	0.09	0.13	0.10
	Stripped	--	--	--
56	Leach	0.13	0.22	0.27
	Filtered	0.23	0.17	0.21
	Stripped	--	--	--

Thus, no conclusions can be made regarding matrix dissolution enhancement as a function of alpha radiolysis. An enhancement in silicon dissolution is observed, however, in similar gamma radiolysis experiments (Pederson and McVay 1983).

Few data are available on the influence of alpha radiolysis on waste form leaching rates without the simultaneous effects of structural damage from alpha bombardment. We have attempted to separate alpha radiolysis from structural damage effects by exposing a borosilicate waste glass for 24 hours at room temperature to a 25μ-thick deionized water film, which was simultaneously exposed to an electroplated film of ^{238}Pu . No enhancement in the rate of growth of the hydrolyzed layer was observed, as determined by secondary ion mass spectrometry depth profiling. Saturation effects may have retarded the leaching rates and masked any effect of alpha radiolysis. Although experiments on the effects of alpha radiolysis on hydrolysis of the matrix of the waste form have not been performed in

brines, the minimal effects observed in other systems would imply that this process is of minor importance. It is emphasized, however, that due to the oxidizing nature of ground waters (particularly brines) exposed to alpha radiation, the effect on actinide solubilities must be addressed.

5.4 RADIATION DAMAGE OF REPOSITORY HOST ROCK

5.4.1 Summary

Because silicate minerals (and metals) are known to be relatively unaffected by gamma radiation (Burns et al. 1982a; Glass 1981), studies on the effects of radiation damage on potential repositories (rock) have focused on salt. Gamma irradiation of salt (NaCl) produces significant structural damage by a recombination of an electron and an electron vacancy on the anion sublattice. Under appropriate conditions of temperature, dose rate, and total dose, colloidal sodium metal is generated. Reaction of brine, which migrates into the repository, with the metallic sodium could possibly generate elevated pH conditions, depending on the fate of the chlorine also formed.

Two aspects of radiation damage in NaCl that have received the most attention are colloid sodium formation (Levy 1983) and stored energy (Jenks and Barr 1977). Although both are radiation-induced, a direct relationship between the two has not been established. In fact, most of the stored energy that is observed in irradiated NaCl is probably associated with induced ionic or molecular defects in the lattice and not with the metallic Na colloids. Thus, the kinetics governing the two phenomena will differ to some extent, as is borne out by the data.

5.4.2 Salt Radiation Damage

5.4.2.1 Colloidal Sodium Formation

Jain and Lidiard (1977) have developed a theory for the growth of colloidal particles in irradiated alkali halides. According to this theoretical model, the maximum rate of colloid formation in NaCl should occur at intermediate temperatures. This maximum in the colloid formation rate has been reported to lie in the 150-175°C region (Levy 1983; Klaffky, Swyer and Levy 1979) for both synthetic and natural NaCl. Near the maximum formation temperature (150°C), the colloid formation (as indicated by the absorption coefficient) decreases with increasing dose rate (Levy 1983). This is most likely the result of the increased fractional recombination

or annealing of defects at the higher dose rates. Based on the available results, it might be expected that at the much lower actual dose rates in a repository, colloid formation could be considerably higher than predicted on the present data base. Additional work on the effects of temperature and dose rate is underway by Levy.

Levy (1983) has found that colloid formation at high doses is proportional to t^n , where t is the irradiation time and the exponent, n , is temperature and impurity dependent. For synthetic NaCl, n varies from 1.5 to 6.2; however, for natural NaCl, n is relatively temperature independent and lies between 1.7 and 2.2. As a result, high colloid concentrations have been estimated with this model under actual repository conditions with as much as 25% of the repository NaCl near the waste canister converted to Na metal colloids. The model, however, ignores the effects of dose rate and any trend toward saturation that may be important. Consequently, further work is needed before actual behavior can be predicted with this model.

Another factor influencing colloid growth is strain. In both synthetic and natural NaCl, strains between 1 and 10% significantly decrease the induction time for colloid formation, presumably by the creation of dislocations which act as nucleation sites (Levy 1983; Jain and Lidiard 1977).

When radiation-damaged salt is dissolved in water, several chemical reactions can be expected (as shown in Table 5.8). In a laboratory time frame, the perchlorate ion may not be seen because it is kinetically limited even though the thermodynamics are extremely favorable. If chlorine gas can escape from the irradiated salt before dissolution, or if the reaction of free chlorine with water is incomplete, the reaction scheme will be dominated by formation of sodium hydroxide and the pH excursions may be expected to be very great, as assumed previously (Levy 1983; Klaffky, Swyer and Levy 1979). Detection of free chlorine liberation from irradiated salts has proved to be a difficult experiment (Levy 1983; Klaffky, Swyer and Levy 1979). However, if no chlorine can escape, each mole of sodium hydroxide will be neutralized by one-half mole strong acid (HCl) and one-half mole weak acid (HOCl), so the pH will be controlled by the salt of a weak acid (the OCl⁻ anion). Certainly in the time frame of a salt repository, the hypochlorite ion (OCl⁻) should disproportionate to the chlorate ion (ClO₃⁻) which is the salt of a strong acid. In that case, the pH should no longer be

TABLE 5.8. Reaction Scheme for Irradiated Salt

$k_1(25^\circ\text{C})$ SLOW

$k_1(75^\circ\text{C})$ MODERATE

$k'_1(100^\circ\text{C})$ VERY SLOW

basic but neutral. Further disproportionation to perchlorate ion (ClO_4^-), also the salt of a strong acid, is not expected to influence the solution pH. Clearly, the fate of chlorine is a key question that remains to be answered in order to understand the long-term effects of gamma-irradiated salt.

Expected solution pH values for one gram of irradiated salt dissolved in 10 ml of deionized water are given in Figure 5.8, where the slopes of curves A and B (linear portions) were calculated from Jenks et al (1975). In curve A it is assumed that all of the chlorine escapes; whereas in curve B, none escapes. Line C assumes that none of the chlorine escapes and that all is converted at least to chlorate ions. These curves also include expected conditions if saturation effects and recombination reactions limit the amount of damage. The results from limited dissolution experiments on solution pH values are included in Figure 5.8. It would appear in these tests that the solution pH is indeed controlled by hypochlorite ion production, as listed in Table 5.8 and Figure 5.8. The pH was higher when the samples were crushed and annealed, possibly as a result of driving off some of the chlorine. This behavior again shows that the fate of chlorine is a key question to be addressed in assessing the chemical implications of radiation damage to salt.

5.4.2.2 Stored Energy

The stored energy of a solid is the difference between the heats of dissolution of irradiated and unirradiated samples as measured by solution calorimetry. This difference is

attributable to radiation-induced damage and reactions in the irradiated sample. According to Jenks and Bopp (1977), the cumulative stored energy in the immediate vicinity of a waste canister in a salt repository should not exceed 250 J/g. They also found, based on laboratory data, that thermally activated annealing will dominate radiation effects at temperatures exceeding 150°C , so that the stored energy should be negligible during the early thermal period. Although data are not available, thermal annealing below 150°C might also be expected over the stored energy accrued in the temperature range from 95 to 144°C , which is slightly lower than the maximum formation temperature for colloids. This is not surprising and simply indicates that different defects may be responsible in the two processes.

5.5 COMPUTER MODELING OF RADIOLYSIS

5.5.1 Summary

The dissolution of nuclear waste forms, corrosion of metallic barriers, and alteration of repository host rocks are highly dependent upon solution species produced from radiolysis of repository ground waters. Computer codes have been developed, and are being continually improved, to predict concentration of radiolytically produced species in simple ground water systems. Time, dose rate, and initial concentration of dissolved ionic and molecular species are parameters that can be varied. Uncertainties in many rate constants for radiation yields used in these calculations and the lack of many appropriate rate constants are major limitations to current

FIGURE 5.8. Effect of Gamma Radiolysis in Acidity (pH) and Oxidation Potential (pe) on Salt Brines. Range of ambient pH and pe values for repository ground waters are shown within the stability field for water (dashed lines) at 25°C.

computational efforts at modeling radiolysis of complex ground waters.

There are only a small number of computer codes currently being used for predicting radiolytically produced species in ground waters. These include the Maxima-Chemist code from Atomic Energy of Canada Limited (Carver, Hanley and Chaplin 1979), the DIFSUB program developed in Denmark and used jointly by the Swedish Nuclear Fuel Safety Program (Christensen and Bjergbakke 1982), and the RADIOL computer code developed at the Pacific Northwest Laboratory (Simonson and Kuhn 1984). The general approach used by these computer codes is to translate the chemical equations of the complete reaction system into a system of ordinary differential equations using the following input data:

- listing of all relevant chemical reactions
- rate constants for these reactions
- yields (G-values) of primary radiolysis products

- initial concentration of all species
- irradiation dose rate
- duration of irradiation.

The derived system of differential equations is then solved by a variety of numerical integration techniques. Concentrations of radiolytically produced species can then be calculated as a function of time, as shown in Figure 5.9, taken from a study of gamma irradiation of a simple brine solution that was performed by Simonson and Kuhn (1984) with the RADIOL program.

There have been encouraging results attempting to verify these computer models with experimental data in simple aqueous systems. Successful application of computer codes to long-term prediction of radiolysis, however, awaits the development of an experimental data base that is broader, more accurate, and more relevant to the complex chemistry of most actual repository ground waters.

FIGURE 5.9. Plot of the Concentrations of Radiolytically Produced Species Versus Time as Predicted by RADIOL at a Dose Rate of 3.5 Mrads/hr and Initial Oxygen Concentration of 1.5 ppm (Simonson and Kuhn 1984)

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CHAPTER 6
PHENOMENOLOGICAL MODELS OF NUCLEAR WASTE
GLASS LEACHING

CHAPTER 6

Phenomenological Models of Nuclear Waste Glass Leaching

ASSIGNMENT: DESCRIBE THE STATUS OF MATHEMATICAL MODELING OF THE LEACHING MECHANISMS FOR NUCLEAR WASTE GLASS

SUMMARY: Data developed in the Leaching Mechanisms Program, and elsewhere, show that continued leaching of waste glass at almost any given set of conditions leads ultimately to steady-state (or quasi-steady-state) concentrations of all leached species. The mathematical models being developed to predict leachant concentration as a function of time depend in varying degrees upon knowing empirically-derived dissolution rate constants, effective diffusion coefficients in the bulk glass and in "protective layers", saturation concentrations for the glass constituents, and the identity of alteration products that form on the glass surface.

Most modeling emphasis has been placed on kinetic behavior during short-term leaching (<1 year), and the fitting of experimental data in this time regime has been achieved successfully in several limited instances. However, no general application of any of the models has as yet been achieved, especially as regards the long-term leaching (hundreds or thousands of years) that is of interest in the context of a geologic repository. Here some models predict (in the absence of waste form-leachant interactions) a $t^{1/2}$ dependence for the leachant concentration growth, others imply a t^1 dependence. Of course, under leachant saturation conditions that will likely obtain in the repository environment, t^0 behavior must be expected.

As part of the Leaching Mechanisms Program, workers at Catholic University have begun development of a phenomenological model that yields a smooth transition in the evolution of the concentration of various species in the leachant from a kinetically-controlled t^1 initial growth to long-term steady-state t^0 behavior. The mathematical structure in which the model is phrased naturally accounts for the transient peaking in the leachant concentrations under slow-flow conditions, and also allows for specifying the static long-term behavior of soluble glass components in terms of a leach-inhibiting protective barrier resulting from saturation with respect to high silica content alteration products formed at the glass surface.

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CHAPTER 6

PHENOMENOLOGICAL MODELS OF NUCLEAR WASTE GLASS LEACHING

6.1 BACKGROUND

Evaluating the potential of glasses for the immobilization of nuclear waste in terms of leach test results assumes that one can make reasonable extrapolations from laboratory experiments made over periods of time from a few months to a few years to repository environment behavior on time scales ranging to tens of thousands of years. For such extrapolations to provide a basis for confident and informed decision making, some structure or framework must be in place that provides an interpretive connection between laboratory and repository time scales. Predictive mathematical models describing material release mechanisms under a wide range of environmental attack conditions are required to provide the needed guidance in this enterprise.

Experimental studies of glass leaching have identified several aspects of the physico-chemical mechanisms that operate in the dissolution of the waste form and should be embodied in these models. In practice, of course, the mathematical statements will be idealizations; they must be established to give general bounds, and should not be expected to provide detailed numerical predictions of long-term repository behavior.

Three rather distinct features of glass leaching must be examined, understood, and integrated into a coherent dynamic picture. The first of these is the mechanism of attack of the aqueous leachant on the glass. The sorts of primitive processes that must be considered and elaborated include corrosion of the glass matrix and diffusion-controlled migration of mobile ions through the matrix to the glass-leachant interface. The second important aspect of the problem is the control of the leaching process by the solubilities of the various glass components in the leachant. Lastly, the impact of an altered surface layer (perhaps resulting from hydration, ion exchange, crystallization or the precipitation of glass constituents

with respect to which the solution is saturated) must be evaluated.^(a)

Of course, these three are not to be regarded as independent; rather, one must examine the interplay of all three, as they interact synergistically, to determine the glass waste form dissolution behavior.

6.2 KINETICS OF AQUEOUS ATTACK

The classical approach to this problem assumes that the initial attack involves the diffusion of mobile ions through the glass network. The basic ideas are set out in Holland's (1966) elegant treatment of glass surface effects. Many of the modern presentations that have been advanced to describe the kinetics of glass dissolution derive their inspiration from this work, and many of the modifications of these ideas can be traced to the seminal work of Godbee and Joy (1974). These authors examine the interdiffusion mechanism in concert with a concentration-dependent dissolution rate and a linear surface layer mass transfer term. They produce an expression for the cumulative amount of material leached that behaves as $t^{1/2}$ for short times and is linear in t for long times.

The crucial step is the combining of mobile-species diffusion with matrix dissolution in a single rational approach. It is rather generally recognized that purely diffusion-controlled kinetics are inadequate to account for the observed leach test data in borosilicate glasses (Kuhn and Peters 1982; Kuhn, Peters and Simonsen 1983). Even when these kinetics are "dressed up" with moving surface boundary conditions (Isard 1982; Wiley 1979) or other suitable accoutrements (Godbee and Joy 1974; Machiels and Pescatore 1981; Cohen 1981), the resulting models do not represent

(a) The necessity for and a description of such an integrated approach has been set out by M. J. Apted (1982).

the fundamental physical and chemical processes that occur. Data such as were presented above in Chapter 1 demand that the model description incorporate diffusion control of the short-time release rates of mobile ion species (such as alkalis) and linear corrosion of the glass network as the limiting feature of the long time dissolution. Of course, such a picture by itself is only credible (and thus can only be tested) under conditions of extreme leachant dilution, i.e., very high flow or leachant renewal rates.

Wallace and Wicks (1983)^(a) and Wicks, Robnett and Rankin (1982) have recently proposed that this dynamic picture must be further modified to include a third mechanism of kinetic control. Their contention is that the early interdiffusion and matrix corrosion stages reach equilibrium quite quickly, after which a protective layer forms on the glass surface (actually on the dealkylized alteration layer created during the initial phase of glass-leachant contact) composed of those insoluble bulk glass components that precipitate from the leachant. Subsequent leaching then requires diffusion through this protective layer.

In describing this mathematically, Wallace and Wicks assume that the interdiffusion process equilibrates so rapidly that it can be ignored in modeling the long-term behavior. Their treatment then considers the glass to be composed of three regions, the unaltered glass, the porous alteration layer, and a protective layer formed by the precipitation of insoluble material at the surface. The thickness of this barrier will increase in time as additional material accumulates as the leaching of the glass continues. Steady-state behavior is achieved when the diffusion of silicon-containing species through this growing precipitate layer balances the rate of silica dissolution. These two rates (per unit area) are:

$$R = K(C_s - C_0), \text{ (dissolution) } (6.1)$$

and

$$R = \frac{D(C_0 - C)}{l}, \text{ (diffusion) } (6.2)$$

where K is the high-dilution rate constant for silica dissolution, D is the silicon

species diffusion coefficient in the protective layer of thickness l . Silica concentrations in the leachant and in the solution adjacent to the porous zone (gel) are designated by C and C_0 , respectively; C_s represents the saturation concentration of silica in the leachant.

Combining these gives a differential equation for Q_{Si} , the amount of silica leached from the glass in time t:

$$\frac{dQ_{Si}}{dt} = \frac{KC_s(1 - \alpha Q_{Si})}{1 + \beta Q_{Si}}. \quad (6.3)$$

Here $\beta = Kq/D$ where q is the proportionality constant in the presumed linear relationship between Q_{Si} and l , and the parameter $\alpha = C_s(S/V)$ with (S/V) being the glass-surface-to-leachant-volume ratio of the system. From this picture Wicks and Wallace derive that in the noninteractive case (described by $\alpha = 0$), the long-time variation of the cumulative amount leached behaves as $t^{1/2}$ rather than as t. They conclude that the transition from corrosion-controlled (or dissolution-controlled) to saturation-controlled leaching behavior is determined by the rate at which silicon-species dissolved at the protective barrier-porous alteration layer interface diffuse through the protective film.

Because experimental leaching data are often presented as a log-log plot of the cumulative amount of a given element leached versus time, and because the slopes of such curves have often been interpreted as being indicative of the leaching mechanism:

slope = 1 -- matrix dissolution,
slope = 0.5 -- layer interdiffusion,
slope = 0 -- leachant saturation,

Wallace and Wicks present the result of their calculation as the time dependence of this slope. Their computation is given in Figure 6.1. It is clear from the figure that β^{-1} characterizes the time scale of the protective layer formation, and thus of the dissolution-to-diffusion transition. Further, except for the case of an open system ($\alpha = 0$) where there is no accumulation of the leaching products, it can be seen that the leachant will eventually become saturated with the slope going sharply to zero.

The central feature of the Wallace-Wicks model is the formation of a protective precipitation layer at the glass gel-leachant interface. Such a layer can be expected to form under interactive conditions, and, as

(a) Also: Wallace and Wicks. "Leachability of Waste Glass Systems--Physical and Mathematical Models." J. Nucl. Mater. (in press).

FIGURE 6.1. Time Dependence of the Slope of the Graph of the Cumulative Amount of Leached Material for Various Degrees of Interactiveness as Measured by the Parameter α/β in the Wallace-Wicks (1983) Model

described in previous chapters of this report, nuclear waste glasses do indeed exhibit precipitates within the hydrated layer (Malow 1982; Lutze et al. 1983; Bunker and Arnold 1983). These precipitates can be hydroxides or more complicated chemical compounds such as analcime, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, or acmite, $\text{NaFeSi}_2\text{O}_6$; their deposition within the porous (gel) layer forms a barrier reducing the rate at which water penetrates this layer, resulting in a reduction of the rate of network breakdown. In particular, it appears that a carefully constructed treatment of the interplay of protective film formation and solubility-controlled dissolution must be incorporated into a realistic model of the leaching process.

6.3 INTERACTIVE MODELING APPROACHES

As outlined in the previous section, models have been developed that characterize leaching in terms of the diffusion of ions through and the dissolution of the glass matrix. Except for the Wallace-Wicks approach, these models emphasize exclusively the properties of the solid waste form; thus they are of limited utility in describing leaching in low or even moderate flow rate environments where the leaching process is a highly interactive one in which there is substantial modification of the contacting aqueous solution arising from glass-leachant interactions. This has prompted the recent development of models in which solubility limitations (Harvey 1983; Plodinec, Jantzen and Wicks 1982; Grambow 1982) and interfacial processes (Wallace and Wicks 1983; Wicks, Robnett and Rankin 1982; Pescatore and Machiels 1982; Machiels and Pescatore 1984; Paul 1982) are treated as the important or even the dominant mechanisms.

Particularly interesting from a phenomenological standpoint is the approach of Harvey

(1983). Generally leach rates are examined as functions of time, flow rate, pH, temperature, etc. Harvey suggests that much of this complication can be eliminated by employing the "gross" solution concentration as the independent variable. For a given glass waste form this generates a master curve, in which the specific dependence on time, flow rate and surface-to-volume ratio are subsumed. The effects of temperature and pH must still be described independently. The specific shape of the master curve is to be derived from an interactive model based on mobile ion diffusion, glass matrix corrosion, and leachant saturation.

The work of Machiels and Pescatore (1982, 1983) expands this modeling approach in which time-dependent interactions are explicitly described. Briefly, the idea is to take into account in a consistent manner:

- a) the migration of mobile ions in the bulk phase
- b) the dissolution of mobile ions, major network formers and network modifiers at the glass-leachant interface
- c) species equilibration in and solid precipitation from the aqueous phase.

This last feature naturally brings about the growth of an altered layer at the glass surface which can, in a time-dependent fashion, modify the rate parameters that characterize diffusion in and corrosion of the surface layer and thus the bulk glass.

This approach has been applied (with some not inconsequential success) to the leaching of a relatively simple (three-component sodium borosilicate) glass in pure water. The rate-determining factor in this case is the

availability of the H_3O^+ species, emphasizing the importance of leachant pH as a governing parameter. As presently constituted the Machiels-Pescatore model does not address the formation of an alteration layer at the glass-water interface, nor has a computer code been employed that accounts for the effects of the reprecipitation of highly insoluble species (e.g., Fe) or of partially soluble major network elements (e.g., Si and Al). Nevertheless, the direction of work that this approach suggests is an entirely logical one to pursue; whether a reasonable extension of the model that includes these currently neglected effects can be obtained, and whether it could then be implemented for a complex multicomponent (say >10 elements) glass, remains an open question.

More recently, Machiels and Sullivan (1983, 1984) have modeled the formation of structurally altered hydration layers. They have investigated the distribution of constituents within these layers by considering five fundamental processes as the operative mechanisms in their development:

1. ion migration due to electrochemical potential gradients,
2. structural alteration reactions resulting in the formation of a transition zone,
3. alteration product formation through precipitation,
4. dissolution of the layer, and
5. generation of an electric double layer at the solution-gel layer boundary.

The model glass system treated is composed of four elements--silicon, sodium, a rare earth element, and a divalent metal--that are representative of major constituents in nuclear waste glasses. As yet this model of surface layer evolution has not been integrated with an approach that accounts for changes in solution chemistry.

The models of Grambow (1982), Kuhn and Peters (1982), and Kuhn, Peters and Simonsen (1983) begin to represent formation of a precipitate layer in this thermodynamic way without invoking any specific dynamic mechanism. Each offers precipitation of insoluble species as the surface layer forming process, but none considers the rate of formation or distribution of precipitates within the layer.

6.4 THERMODYNAMIC MODELS

Most of the models developed to describe the leaching behavior of glass are kinetic models, attempting to account for the dependence of the dissolution kinetics of glasses starting with the time when the dry surface of the glass first comes in contact with the aqueous leachant. However, as noted above, in nuclear waste applications contact times are likely to be very long and the leachant composition is thus determined by saturation with respect to surface precipitate phases.

Consequently, a reasonable alternative to developing a full dynamic treatment is to ignore the kinetic aspects of the leaching process entirely, and to regard equilibrium thermodynamic considerations as being the factors of overriding importance. Several such models are summarized below.

According to Grambow (1982) the leaching of nuclear waste glasses exhibits two main aspects. Without solubility restrictions, congruent leaching occurs at all pH values and leachant compositions. When this reaction raises the solution concentration levels of certain elements to the level at which new solid phases form, these will regulate the leachant composition. These solid phases are dominant constituents of the leached layer. For instance, in the leaching of PNL 76-68 glass, the solubilities of the reaction products regulate the solution concentration as if it were in equilibrium with such solids as pure $Fe(OH)_3$ (amorphous), $Zn(OH)_2$ (amorphous), $Nd(OH)_3$, $SrCO_3$ and $CaCO_3$. The experimental conditions--in particular, the pH value--that govern the formation of solid reaction products and control the solution concentration can be identified. By assuming initial congruent dissolution and then identifying the solubility-controlling solid phases, Grambow has constructed a set of reaction path diagrams that describe the leaching of PNL 76-68 glass.

A strictly thermodynamic approach to the analysis of glass durability has been developed by Plodinec, Jantzen and Wicks (1982) following the lead of Paul (1982). The glass is treated as a mixture of species such as Na_2SiO_3 , SiO_2 , Fe_2O_3 , ... which have known free energies of hydration. The stability of the glass toward aqueous attack is then assumed to be measured by the sum of these component hydration free energies, each weighted by the mole fraction of the corresponding component in the glass (a mathematically more

sophisticated version of this idea is elaborated in the following chapter). This calculated free energy gives a durability measure that depends on the composition of the glass. To test this idea, the authors performed static leaching studies (90°C, deionized water, 28 days, MCC-1 procedures) on glasses chosen from a wide range of compositions: 35 to 70% SiO₂, 0 to 13% Na₂O, ... The normalized silicon release (corrected in the case of highly alkaline glasses to account approximately for the pH rise during the measurement) is examined as a function of the calculated free energy of hydration.

Several points of weakness would appear to legislate against expecting quantitative predictions from this approach. The choice of structural units in calculating free energies of hydration is arbitrary. Species inter-

actions, such as the formation of aluminosilicates, are ignored. In addition the application of equilibrium thermodynamic considerations to a fundamentally dynamic situation is only justifiable *post hoc*, especially in establishing a relationship between the hydration free energy and the activation energy for aqueous dissolution. On the experimental side, the use of MCC-1 test results giving dissolution data over a fixed period of time, rather than at some definite stage of interaction between the glasses and the contacting solution, is apt to skew the model validation attempt.

Despite these limitations, the Plodinec-Jantzen-Wicks approach leads to a linear correlation (see Figure 6.2) between the normalized loss of silicon and the calculated

FIGURE 6.2. Release of Structural Silicon as a Function of the Glass Hydration Energy (Plodinec, Jantzen and Wicks 1982)

free energy of hydration. This is an especially impressive achievement in view of the disparity of materials studied--including waste glasses, frit glasses, medieval glasses and natural glasses whose Si losses differ by a factor greater than 300.

6.5 REACTION KINETIC MODELS

For the past decade, members of the geochemical community have been concerned with the kinetics of rock weathering and mineral dissolution under near-earth surface conditions. Many of the minerals of interest are silicates and the temperatures and pressures are not dramatically different from those relevant to the description of a nuclear waste repository. It is of interest to compare the dissolution kinetics of crystalline silicates with the dissolution of glasses in part because silicates appear as crystallized reaction products from the recrystallization of the gel layer and in part because framework silicates have local structures similar to the local structure of silicate glasses.

Models for the dissolution of glasses evolved naturally from considerations of control by solid-state diffusion through a depleted leach layer that was formerly part of the glass or through a protective layer deposited on the surface of the glass. The geochemists took as their starting point the traditional theory of reaction kinetics and from these classical ideas, constructed models appropriate to the dissolution of silicate materials (Lasaga and Kirkpatrick 1981).

Heterogeneous reactions such as mineral dissolution occur at the interface between the dissolving crystal and the aqueous solution. The general steps involved in any such reaction are:

1. transport of reactants to the solid surface,
2. adsorption of the reactants,
3. chemical reaction between some aggressive species in solution and some point of attack on the crystal surface (the detailed atomistic chemistry can be quite complex),
4. desorption of products, and
5. transport of products into the bulk solution.

For a chain of individual reaction steps, the slowest step limits the overall rate. In general, control has been ascribed to either

transport (steps 1 and 5) or to surface reaction kinetics (step 3).

In a transport-controlled reaction, the surface chemical kinetics are fast so that migration of ions through the solution in the fluid boundary layer becomes rate-limiting. In classical Nernst theory the change in concentration is simply the flux, j , of material across the boundary layer which in turn is controlled by the layer thickness, δ , and the diffusivity, D , of ions in the liquid. The driving force is supplied by the concentration gradient.

$$\frac{dC}{dt} = \frac{S_i}{V} = \frac{DS}{\delta V} (C_s - C) = k_T (C_s - C) \quad (6.4)$$

where k_T is a mass transfer coefficient. The integrated form of the equation is

$$C(t) = C_s (1 - e^{-k_T t}). \quad (6.5)$$

Empirically, it is found that dissolution of substances with solubilities greater than 10^{-4} moles/liter is usually mass transport limited while dissolution is surface reaction controlled for substances with solubilities less than 10^{-5} moles/liter (Berner 1978). Nuclear waste materials would be expected to dissolve by surface reaction controlled mechanisms.

Providing that the dissolving solid will eventually come to equilibrium (saturation) with the solution, the bulk rate equation is written

$$\frac{dC}{dt} = \frac{S}{V} k_s (C_s - C)^n \quad (6.6)$$

The exponent, n , is the order of the reaction and k_s is a reaction rate constant. An alternate expression for ionic solids is (Berner 1978)

$$\text{Rate} = \frac{V}{S} \frac{dC}{dt} = k(1 - \Omega)^n \quad (6.7)$$

where Ω is the saturation ratio defined as

$$\Omega = \frac{\text{ion activity product}}{\text{solubility product constant}} \quad (6.8)$$

If $n = 1$ (first order kinetics), Equation 6.6 can be integrated to give

$$C(t) = \frac{S}{V} C_s (1 - e^{-k_T t}) \quad (6.9)$$

The same form is obtained from transport theory but with a much different definition of k_s . The rate constants in this formulation have units of $(\text{time})^{-1}$ and can be replaced by a characteristic reaction time τ which is a measure of the response time of the system. First-order reactions are found for those systems where one of the concentration variables is dominant and where there is a one-to-one atomic reaction at the surface, for example the exchange of an alkali ion by a proton. Higher-order reactions are often observed. The competing rates of both forward and back reactions are incorporated in Equation 6.6. An initial rapid rate, expressing mainly the forward reaction, decreases so that the concentration time function curves over to become asymptotic to the horizontal line marking the saturation concentration.

Many minerals cannot exist in equilibrium with aqueous solutions under near-surface temperatures and pressures. Examples are the alkali and alkaline earth aluminum silicates whose three-dimensional framework structures have much in common with the structural backbone of silicate glasses. For these substances, the back reaction is not usually observed. The trend toward metastable equilibrium is cut off by the precipitation of new, lower-solubility product phases. The product phases are usually hydrated and can be regarded as the reaction products of the original phase with water. The system is then described by two reactions and two rate equations. The forward reaction is the dissolution of the primary phase. Instead of a back reaction, there is a precipitation reaction which because it removes ions from solution is often treated as a back reaction.

Because dissolution of the metastable phases takes place far from equilibrium, the forward reaction rate is little influenced by the build-up of reaction products in solution and obeys zero-order kinetics. That is

$$\frac{dC}{dt} = \frac{S}{V} k_+ \quad (6.10)$$

The precipitation reactions can be taken separately so that the net concentration of ions in solution is given by

$$\frac{dC}{dt} = \frac{S}{V} k_+ - \frac{A'}{V} k_- (C - C_{sp}) \quad (6.11)$$

where A' is the effective surface area of the precipitates, k_+ is the forward reaction rate constant, and k_- is the precipitation rate

constant. $(C - C_{sp})$ is the supersaturation with respect to the precipitate phase.

The dissolution of silicates varies with pH. Hydrogen ion activity can be factored specifically into the rate equations:

$$\frac{dC}{dt} = \frac{S}{V} k'_+ (a_{H^+})^n - \frac{A'}{V} k_- (C - C_{sp}) \quad (6.12)$$

The exponent, n , is unity for most minerals in the acid regime. In basic solutions $-0.2 > n > 0.6$.

When the dissolution kinetics of silicate minerals were first examined, the concentration-time curves appeared to be parabolic and it was assumed that the rate-controlling feature was a barrier layer built up on the surface, analogous to the layers that had been observed on glasses (Helgeson 1971; Petrovic 1976). However, when later workers looked for the surface layers with increasingly sophisticated characterization methods, the layers were not found. The initial rapid rate appears to be due to dissolution of small particles attached to the surface of mineral grains, and solution attack on high energy sites on the crystal surface such as dislocation sites, grain boundaries, and cleavage cracks. When these are consumed, the rate slows down to that of the bulk materials but the overall rate curve gives a misleading impression of parabolic kinetics. When the effect of changing surface activity is taken into account most silicate minerals so far examined dissolve by a linear kinetics mechanism (Grandstaff 1978; Berner and Holdren 1979).

The rate of dissolution of silicate minerals is strongly dependent on the silicate structure. Table 6.1 gives some rates calculated by Lasaga (1984) at 25°C and at pH = 5.0. The relative instability of nepheline and the role of aluminum in forming less reactive materials is apparent from the constants in the table.

6.6 MATHEMATICAL PHENOMENOLOGY OF GLASS LEACHING: A NON-MECHANISTIC MODEL

As an alternative to either a kinetic or thermodynamic model based on mechanistic and/or chemical equilibrium considerations (such as diffusion, dissolution, layer formation, solubility limitations and precipitation), one can describe glass leaching by generating a mathematical structure in which specific process details are absorbed in parameterized response functions that are

TABLE 6.1. Rate of Release of Silica at 25°C and pH = 5

Mineral	Composition	Rate ₂ (moles/cm ² /day)
Quartz	SiO ₂	8.64 x 10 ⁻¹³
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	2.16 x 10 ⁻¹²
K-Feldspar	KAlSi ₃ O ₈	1.47 x 10 ⁻¹¹
Diopside	CaMgSi ₂ O ₆	1.2 x 10 ⁻⁹
Forsterite	Mg ₂ SiO ₄	1.08 x 10 ⁻⁸
Nepheline	NaAlSi ₃ O ₈	2.4 x 10 ⁻⁸

used in this theoretical framework. In addition, this mathematical structure can be generalized so that leach test configurations other than static testing, e.g., continuous flow or periodic fractional leachant renewal tests, can be accommodated and analyzed.

As a part of the Leaching Mechanisms Program, Montrose, Macedo and Barkatt (1984) have developed such a phenomenological approach to account for the results of tests in which the glass specimen is immersed in a flowing leachant. The aim is to obtain expressions for the time-dependent accumulation of leaching products in the contacting solution, as well as to obtain the steady-state results as a function of flow-rate or residence time. The residence time or renewal time T_r is defined as the time required for a complete replacement of the volume of the leachant, either due to continuous flow or to periodic fractional leachant replacement. Examples of the type of data to be described are shown in Figures 6.3 and 6.4.

In Figure 6.3 are shown two sets of curves of the time dependence of the leachant concentrations of Na, B and Si for different leachant renewal times (or flow rates). These data (obtained under rather slow flow conditions) are noteworthy in that they highlight the "concentration overshoot" phenomenon that can be taken as indicating the presence of a protective layer at the glass-leachant interface. In contrast to this, leaching studies at high flow rates are not marked by the peaking of the concentration; the (approximately linear) rise at short times smoothly and monotonically evolves into a constant steady-state limiting value at long times.

Figure 6.4 shows the dependence on leachant renewal times, or flow rate ($\propto 1/T_r$), of these long time limiting concentrations. Note that the ordinate here is "normalized concentra-

FIGURE 6.3. Typical Data Showing the Accumulation of Leached Material in the Leachant as a Function of Time After Immersion for Two Different Renewal Times (Flow Rates). These results are from data presented in Chapter 1 for SRL-131 glass in DI water at 70°C.

FIGURE 6.4. Typical Data Showing the Limiting ($t \rightarrow \infty$) Steady-State Concentrations of Leached Material as a Function of Leachant Renewal Time (Flow Rate). Results are from the same source as those in Figure 6.3.

tion," meaning that the actual leachant composition is divided by the mole fraction of the given element present in the glass specimen. Such a normalization procedure causes all the low T_r data (the high flow data) to fall on a single curve, indicating congruent leaching under these conditions.

The features of the results that the model should reproduce are most easily enumerated by examining separately the behavior in the noninteractive (high flow) and strongly interactive (low flow) regimes. Different phenomena and processes predominate in these two situations; the aim is to derive each as the limiting behavior of a single generalized picture.

Consider first the noninteractive region wherein high dilution conditions always obtain in the leachant. The principal features of the data include the following:

1. Leachant concentrations exhibit a linear increase with contact time in a static test in a very large leaching bath, or equivalently in a flow test for total immersion times $t \ll T_r$, where T_r is the characteristic leachant renewal time (or residence time). Specifically, the concentration of the i th constituent increases as

$$C_i(t) - L_i(S/V)t \equiv A_i t,$$

where L_i is the leach rate of the i th species and S/V is the glass surface-to-leachant volume ratio.

2. For immersion times $t \gg T_r$, the concentration in solution becomes independent of time. The increase in the amount of material in the leachant is just balanced by the removal of material owing to flow. The long-time limiting concentration is

$$C(t \rightarrow \infty) \equiv C_\infty = AT_r,$$

where the subscript "i" has been suppressed for the sake of simplicity.

3. In a continuous flow situation, the growth of the leachant concentration in time is given by

$$C(t) - C_\infty (1 - e^{-t/T_r}).$$

In a pulsed-flow test in which a small fraction of the leachant $f = \Delta V/V \ll 1$ is exchanged at intervals fT_r , the corresponding expression for the concentration after n exchanges is obtained by the replacement $t/T_r \rightarrow nf$.

In the highly interactive, low flow (large T_r) region, solubility limitations rather than dynamic mechanisms determine the long-time leaching behavior. Several features of the time dependence of the leachant concentration are characteristic.

1. At short times ($t \ll T_r$), the concentration of the contacting solution grows as

$$C(t) = At$$

just as in the noninteractive case, since the leachant has not as yet been significantly affected by glass dissolution.

2. At long times ($t \gg T_r$), the concentration becomes time independent at a value $C_s < AT_r$ determined by the solubility limit of the species; attack by the contacting solution on the glass waste form is reduced to a rate just sufficient to maintain this concentration in the presence of leachant removal due to flow.
3. Except at the very low flow rates, the shapes of the $C(t)$ versus t plots are not qualitatively much different from the exponential form typical of the high flow domain. However, at very low flow rates the shape is rather dramatically altered. Following the initial linear rise, the concentration reaches a maximum value and then decreases before finally leveling off at its long-time steady-state value.

There are several ways in which the "concentration overshoot" can be viewed. When the dissolution is relatively fast compared to the rate at which insoluble compounds are formed, there is a transient domain in which the solution will be supersaturated with respect to the precipitates, before finally reaching the saturation composition. Such an interpretation is perhaps not implausible in considering the Si leaching behavior, but cannot be seriously maintained as an explanation for the behavior of highly soluble species such as B.

Alternatively, one can interpret the overshoot as representing a time-dependence of the saturation limit as glass-leachant interactions modify the nature of the alteration products on the glass surface. This latter picture, quite similar to that proposed by Apted (1982), is almost certainly a more accurate portrayal of the situation than the former. The major clue to this is that both the overshoot and saturation-like behavior are observed for an element such as boron for which the formation of insoluble precipitates seems extremely unlikely. It appears that the initial dissolution of the glass leads to the formation of a hydrated alteration layer; this is followed by the precipitation from solution of insoluble species, which deposit in the porous alteration layer to form a protective barrier limiting

the attack of the glass by the solution. Steady state is achieved when the thickness of the protective layer has grown to a point when the transport of attacking water through it by diffusion has slowed so that its continued growth is just balanced by the dissolution of the glass that forms it. The picture that emerges--essentially that of Wicks and Wallace with the extra feature of protective layer dissolution--is shown schematically in Figure 6.5. The fundamental conclusion as stated in Chapter 1 of this report is that:

...the altered surface layer formed at slow flow rates has a different character than the "classical" diffusion-limiting hydration layer and that it evolves subsequent to, rather than prior to, a process of linear, congruent dissolution. Nonetheless, this altered layer can be termed "protective" in the general sense of a surface region which limits the rate of material loss, since the alteration process is observed to result in considerable retardation of the rate of accumulation of even the most soluble glass components (boron, alkalis) in the aqueous phase...

This view contrasts rather sharply with the conclusions of Aagard and Helgeson (1982), who argue that the dissolution rate of silicate minerals is governed by hydrolysis reaction kinetics at the surface. In their picture mass transport via diffusion across a protective film does little to determine the dynamic behavior.

FIGURE 6.5. Schematic Diagram of the Alteration Layers at the Glass-Leachant Interface

The mathematical framework needed to describe this sequential behavior, dissolution - precipitation - retardation - dissolution - saturation, is rather easily generated. In contrast to the mechanistic approach described in the preceding section, we choose a representation that gives a mathematical description into which one's intuition and conclusions regarding the importance of specific processes can be injected at the end; the basic idea is to write the leachant concentration at time t after the immersion of the glass as an integral over the net accumulation rate during the interval 0 to t :

$$C(t) = \int_0^t dt_0 G(t_0) \quad (6.13)$$

In the idealized noninteractive case (ignoring the early interdiffusion process) $G(t_0) = A$ under static infinite dilution test conditions; in a flow test the appropriate form is

$$C(t) = \int_0^t dt_0 G(t-t_0) e^{-t_0/T_r} \quad (6.14)$$

The interactive case is treated by recognizing that the leaching characteristics of the system are described by $G(t-t_0)$ and this is dependent upon the time-varying concentration of the leachant and the evolving alteration layer at the glass surface. Generally one may write

$$G(t-t_0) = G_0(t-t_0) \{1 - \lambda \int_0^t dt_1 G_1(t-t_1)\} \quad (6.15)$$

$$+ \lambda^2 \int_0^t dt_1 \int_0^t dt_2 G_2(t-t_2, t-t_1) \dots$$

Here λ is a parameter measuring the extent of the interactive behavior, i.e., the degree to which changes in the nature of the glass and the leachant (owing to leaching) affect the (continued) glass leaching characteristics, and the functions $G_n(t-t_n, t-t_{n-1}, \dots, t-t_1)$ give the n^{th} order time response of the glass-leachant system to the interaction. The basic idea is that in the linear or non-interactive situation the leachant concentration at time t is the result of the superposition of incremental changes initiated at times $0 \leq t_0, t_1, t_2 \dots \leq t$; the non-linear interactive situation requires that the joint contributions of incremental pairs (e.g., of the changes at t_1 and t_2), triplets, etc., be considered. These multiplet contributions correspond to the terms in Equation 6.15.

Montrose, Macedo and Barkatt (1984) take an elementary product form for the non-linear response functions as a first approximation:

$$G_n(t-t_n, \dots, t-t_1) = f(t-t_n) \dots f(t-t_1), \quad (6.16)$$

which gives

$$G(t-t_0) = \lambda \sum_{n=0}^{\infty} (-\lambda)^n \left[\int_0^t dt_1 f(t-t_1) \right]^n, \quad (6.17)$$

or

$$G(t-t_0) = \frac{\lambda}{1 + \lambda \int_0^t dt_1 f(t_1)} \quad (6.18)$$

With the help of (6.14) this gives:

$$C(t) = \frac{AT_r (1 - e^{-t/T_r})}{1 + \lambda \int_0^t dt_1 f(t_1)} \quad (6.19)$$

The steady-state limit is

$$C(t \rightarrow \infty) = \frac{AT_r}{1 + \lambda T_r / C_s}, \quad (6.20)$$

which implies $\lambda = AT_r / C_s \int_0^{\infty} dt_1 f(t_1)$. Equations 6.19 and 6.20 with $f(t_1) = \exp(-t_1/\tau)$ are used by Montrose, Macedo and Barkatt (1984) to represent the leaching data obtained in flow tests. Sample fits of these expressions to measurements in a borosilicate waste glass (SRL TDS-131) are shown in Figures 6.6 and 6.7.

It is clear that the simplifying assumptions embodied in Equation 6.16 and the exponential decay form for $f(t_1)$ represent a drastic oversimplification of the actual situation. It is obvious that using a somewhat more complicated form for $G_n(t-t_n, t-t_{n-1}, \dots, t-t_1)$ will improve the quality of the fits to experimental data, as well as allowing for a more physically appealing and realistic picture of the leaching process. Basically one would try to construct $G(t-t_0)$ in a quasi-mechanistic fashion; certainly it is imperative to include a second dynamic parameter (r being the first) to characterize the diffusion-controlled transport across the protective surface layer that forms under slow leachant flow (large T_r) conditions.

One important feature of the description that is lacking is a quantitative prescription for

FIGURE 6.6. Fits of Some of the Data Given in Figure 6.3 to the Form of Equation 19

evaluating the long-time limiting concentrations of the various elements. For example, while the short-time and high flow rate leaching of both the DWRG and SRL TDS-131 glass is adequately described as congruent corrosion, the limiting concentrations of, say, boron, sodium and silicon can be predicted and related only if one can identify the silicate compounds that form on the glass surface, and govern the saturation of the contacting solution. Macedo and co-workers (based on work such as that of Paces 1973 and 1978) have obtained reasonably accurate estimates of the saturation concentrations of Si by using the solubility of crystalline quartz and attempting to make a reasonable adjustment for the pH rise that occurs during the leaching process. Such a procedure is in rather good agreement with the ideas presented in Chapter 7.

6.7 DIFFUSION-CONTROLLED DISPERSION OF LEACH PRODUCTS

The removal of dissolved species from the immediate neighborhood of a glass waste form under aqueous attack is normally accomplished by the bulk motion of the flowing ground water (advection). In a completely stagnant ground water environment this mechanism is absent, and the dispersion of the dissolved species occurs via diffusion. The role of

FIGURE 6.7. Fits of Some of the Data Given in Figure 6.4 to the Form of Equation 20

this in waste glass leaching has been discussed by Hughes, Marples, and Stoneham (1983). Anderson (1980) and Shepherd and Cherry (1982), in the context of the migration of contaminants from uranium mill tailings, have also given rather thorough reviews of this phenomenon. In discussing the waste form leaching problem, the principal effect of diffusion of dissolved species through the ground water is to establish a maximum effective leachant renewal time (equivalently, a minimum effective flow rate). If this minimal renewal rate is one that is accessible experimentally, then it becomes possible to conduct tests over the entire range of repository-significant flow conditions, and thus to explore all of the important flow-dependent leach mechanisms.

The appropriate expression connecting the maximum effective leachant renewal time, $t_{r,max}$ and the diffusion coefficient in the contacting ground water D_w can be inferred from the work of Hughes, Marples, and Stoneham (1983) as

$$T_{r,max} = \xi^2 / \gamma D_w \quad (6.21)$$

where ξ is a characteristic dimension of the glass waste form, and γ is a geometrical factor of order unity. They use the equivalent of this formula with $\xi = 1$ m and $\gamma = 1$ and a diffusion coefficient of 1×10^{-11} cm²/sec $\approx 1 \times 10^{-6}$ cm²/day to obtain a minimum effective flow rate of about 5×10^{-4} cm³/day

(this corresponds to a value $\approx 10^{10}$ days for $T_{r,max}$), which is extremely small. The value of D_w used by Hughes et al. was inferred from a burial experiment (Merritt 1976) wherein an effective leach rate of 5×10^{-11} g-cm²-day⁻¹ was obtained. Such a leach rate seems astonishingly small and thus leads to an unreasonably small value of D_w , one that is more characteristic of solid, rather than liquid, state diffusion. Consequently, the computed value of $T_{r,max}$ is larger than one would expect.

A more realistic estimate of D_w , say, 2×10^{-5} cm²/sec ≈ 2 cm²/day (a value typical of diffusion in water) gives $T_{r,max} = 5000$ days, corresponding to a pore velocity (linear flow rate) of about 0.1 m/yr, which is much more in line with one's intuition about dispersive time scales.

Chambré, Pigford and their co-workers (1982a,b,c; also Waste Isolation Systems Panel 1983) have explored in detail this situation in which the contacting ground water has reached saturation, and thus the glass dissolution rate is controlled by mass transfer from the waste by diffusion and convection. Of relevance here is their analysis of the release rates from glassy waste forms in a ground water flow field in which the glass is considered as an impenetrable monolith. For a long cylindrical (radius = a) waste form, the volume of water that presents the resistance to diffusive and convective transport is confined in a relatively thin

boundary layer in contact with the glass at flow velocities > 1 m/year. The difference between the Chambré et al. flow mechanism and that treated previously in this paper is illustrated in Figure 6.8. Whereas the previous descriptions assume a severely fractured (almost pulverized) glass waste form through which there is rather free ground water flow, the situation described in these few paragraphs deals with a nearly intact waste form around which the flow must take place.

Chambré, Pigford, et al. present their results in terms of a fractional annual release rate θ for saturation conditions. They distinguish high and low flow cases in terms of a dimensionless Peclet number

$$Pe \equiv Ua/D_j$$

For relatively high flow velocities ($Pe > 4$, which corresponds to $U > 1$ m/year to $T_r <$

FIGURE 6.8. Schematic Representation of the Ground Water Flow Field and Contaminated Ground Water Plume for (a) the Case of an Essentially Intact Waste Form, as Considered by Pigford and Coworkers; and (b) the Case of a Severely Fractured Waste Form

5 year) they obtain for the j^{th} species) (Chambré, Pigford and Zavoshy 1982a)

$$\theta_j = \frac{C_s(j)}{x_j \rho} \cdot \frac{8 \epsilon U a}{\pi a^2} = \frac{C_s(j)}{x_j \rho} \frac{8 \epsilon U D_j}{(\pi a)^{3/2}} \quad (U > 4 D_j / a) \quad (6.22)$$

where $C_s(j)$ is the saturation concentration, x_j is the mass fraction of species j in the glass and ρ is the bulk density of the glass. At zero velocity ($Pe \ll 1$) the fractional release for a prolate spheroid is given by (Chambré, Pigford and Zavoshy 1982b)

$$\theta_j = \frac{C_s(j)}{x_j \rho} \frac{\gamma \epsilon D_j}{\xi^2} \quad (U = 0) \quad (6.23)$$

where, as in Equation 6.21, γ is a geometrical factor of order unity and ξ is a characteristic dimension of the waste form. From this we have estimated an equivalent maximum residence time. The result is just

$$T_{r, \max} = \frac{\xi^2}{\gamma \epsilon D_j} \quad (6.24)$$

which is, apart from the explicitly displayed tortuosity factor, the same result as was given above. If this factor is set to unity, then (as above) one gets $T_{r, \max} = 5000$ days. Even if it is assumed that backfill and geologic barriers provide an impediment to dissolved species diffusion such that a value of ϵ of about 10 to 20% is appropriate (Cherry et al. 1979), the resulting $T_{r, \max}$ is not of an unreasonable order of magnitude. In a laboratory test where relatively large glass surface-to-leachant volume ratios ($> 1000 \text{ m}^{-1}$ or so) can be employed, this translates to a residence time $T_r = 100$ days (if $\epsilon = 1\%$) and 1000 days (if $\epsilon = 10\%$).

Moreover, while this would certainly stretch the limits of laboratory studies, it does not present an unmanageable experimental challenge. Therefore, it is possible to carry out leaching tests and to assess model predictions for conditions that completely span the relevant spectrum of leachant flow rates.

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CHAPTER 7
PROTOCOL, A NUMERICAL SIMULATOR FOR GLASS
DISSOLUTION

CHAPTER 7

PROTOCOL, a Numerical Simulator for Glass Dissolution

ASSIGNMENT: DEVELOP THE COMPUTER CODE PROTOCOL AND ITS APPLICATION TO THE SIMULATION OF THE DISSOLUTION REACTIONS OF NUCLEAR WASTE GLASSES BY GROUND WATERS.

SUMMARY: A FORTRAN version of PROTOCOL, including subroutines for online graphics, is set up on the CRAY-1 at Lawrence Livermore National Laboratory, and can be accessed through arrangements with the U.S. DOE. The code contains 1) a kinetic capability to describe release from the glass, 2) an equilibrium capability based on the geochemical code MINEQL that models solution concentrations and precipitate formation, 3) a system monitoring capability that directs the computations through a series of discrete time increments, and 4) a capability to estimate the standard Gibbs free energy function of poorly characterized solid phases.

Within the constraints of available data, PROTOCOL has achieved its intended purpose. It has been developed into a flexible instrument for the evaluation of both experimental and theoretical approaches to the dissolution of solids. Conventional solubility considerations are also extended to non-stoichiometric alteration products of glasses. Many of the precipitates that form in leaching of waste glass are as yet unidentified, hydrous, poorly-ordered species that cannot be accommodated by the standard thermodynamics-based geochemical code. PROTOCOL contains a subroutine based on modifications of Y. Tardy and R. M. Garrels ("A Method of Estimating the Gibbs Energies of Formation of Layer Silicates," *Geochim et Cosmochim Acta*, 38:1106-1116, 1974) that shows promise of identifying thermodynamic "building blocks" from which the hydrous precipitates in the leached surface layer may be assumed to be composed in varying combinations.

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CHAPTER 7

PROTOCOL, A NUMERICAL SIMULATOR FOR GLASS DISSOLUTION

7.1 DESCRIPTION

7.1.1 Concept

As described in the preceding chapters of this report, much of the work performed under the Leaching Mechanisms Program has consisted of laboratory investigations. However, intensive efforts have also been directed toward the development of a unifying predictive computer code. The objective in developing such a code, called PROTOCOL (PROgram TO COrrelate Leaching data) was to provide a means for predicting the long-term leaching behavior of waste glasses. The code is now fully operational at Lawrence Livermore National Laboratory.

PROTOCOL is a general-purpose numerical simulator for the dissolution reactions of solids with aqueous solutions, specifically applied to the potential corrosion of nuclear waste glasses by ground waters. The motivation for its development is the observation that while very durable waste forms have been developed, the complexities of leaching processes make it desirable to develop improved methods of quantitatively extrapolating experimental rate data to very long reaction times in a repository environment.

As described in Chapter 6, there are at least three types of models for interpreting and predicting the dissolution of waste glasses: mechanistic models (Wallace and Wicks 1983), thermodynamic stability models (Granbow 1982; Plodinec, Jantzen and Wicks 1982), and phenomenological mathematical models (Chapter 6 of this report). PROTOCOL has been designed to accept any of these three types of models as initial input; in fact, PROTOCOL provides a means for comparing the predicted output from these various leaching models. PROTOCOL also offers a vehicle for comparing the theoretical output from any given leaching model to the actual results of experimental leaching studies. Finally, in addition to these functions of interpreting experimental information and model results, PROTOCOL serves as an interface between the experiment and the

chemical performance of a waste form in a geologic repository.

PROTOCOL was developed in close association with the experimenters in the Leaching Mechanisms Program. As a result, PROTOCOL was specifically designed to accept real time as an input parameter. Similarly, it can yield predictive output in terms of real time. This feature tends to set PROTOCOL apart from more traditional reaction-path geochemical codes, such as PHREEQE (Parkhurst, Thorstenson and Plummer 1980; Noronha and Pearson 1983) and EQ3/6 (Wolery 1979; Lawrence Livermore National Laboratory 1983). Later in this chapter an example of real-time kinetic input and output are given for the dissolution of silica. PROTOCOL may be thought of as a reaction-path code in the sense that it simulates a system that is evolving chemically in a series of discrete progressive states at specified real-time intervals.

For simple glasses dissolving in simple environments, closed-form rate and solubility functions are generally adequate and convenient. As glass/water systems become more chemically complex however, such functions become increasingly tedious to derive and evaluate. The progress of dissolution at the early times that are most accessible experimentally seems to be determined by the interactions of many parameters, some of them quite subtle. A basic premise of PROTOCOL is that leaching is a system-specific process, in which values for all parameters may be interrelated.

In the aqueous corrosion of durable solids, there is a considerable disparity between mass transfer rates across the liquid-solid interface and in the bulk aqueous phase. This has suggested the possibility of a composite model in which the phases are monitored separately as two quasi-independent systems that are coupled at the interface. That is, solid phases act as mass generators and the aqueous phase acts as a receiver, in

which a redistribution of material takes place at a relatively high rate.

In simulation, such an evolving system is approximated by evaluating the results of mass transfer and chemical reaction in a sequence of time increments. The results of chemical redistribution provide feedback to the leaching rate functions, where values for such parameters as aqueous activities may be required. Depending on the resolution required and the rates of change of the various contributing functions, large numbers of calculations may be required, and this approach is feasible only with computer techniques.

Since the values of the various model parameters can be specified over very wide ranges, leaching data can be used to predict dissolution and release in systems that are not experimentally accessible, such as a full-scale, operating waste repository.

PROTOCOL has three general attributes: a kinetic capability, a thermodynamic capability and a managerial function. The managerial function integrates these chemical activities into a consistent simulation of a dynamic, composite process.

In addition to the thermochemical capabilities of geochemical codes, a feature has been added which we believe is unique to PROTOCOL; the ability to estimate the standard free energies of formation of the poorly-defined amorphous and cryptocrystalline solids which form on the surface of waste glasses as a result of leaching. The standard free energies are estimated by back-calculation from the steady-state concentrations of dissolved species observed during leaching experiments.

Although a great many geochemical computer codes are already available to the scientific community (see, for example, the extensive listing of such codes in Nordstrom et al. (1980), we believe the PROTOCOL has several characteristics which will make it especially valuable to researchers in the field of nuclear waste disposal. PROTOCOL should also be of interest to workers in many other fields, such as the weathering of rocks and minerals, formation of ore deposits, and diagenesis of sediments.

7.1.2 Scope

PROTOCOL is a pragmatic chemical model, in that it has been designed to make use of very diverse experimental and theoretical information about the processes of glass dissolution and about the systems in which they occur.

As suggested previously, dissolution is system-specific, and must be described quantitatively in terms of a set of system parameters. This set includes solid and aqueous chemical composition, temperature, interfacial area, water flow rate and resident water volume. Solid composition includes phase identity, crystallinity, concentrations of chemical components and thermodynamic stability. Aqueous composition includes activities of chemical species, pH and Eh.

In addition to single phase glasses and crystalline products, two other types of solid materials can be considered by the model: multiphase waste forms and non-ideal product phases. Although waste glasses may well be produced as single phases, the flexibility has been retained to handle multiphase dissolution, where components can be leached from different sources at different rates. In the studies of glasses this option has not been exercised.

At low or slightly elevated temperatures, the slow kinetics of ordering often prevent the formation of thermodynamically stable crystalline product phases. A procedure has been included to estimate the stabilities of non-ideal and amorphous phases that may actually be formed. This will be discussed in greater detail in the summary of available options and in the discussion of the thermodynamics of surface products.

The PROTOCOL model assumes that some processes that may be significant in dissolution such as rates of solid phase ordering, diffusion, adsorption, ion exchange and aqueous polymer formation can at this time best be described by experimentally-based dissolution rate functions. However, whenever more fundamental descriptions can be developed, these can be readily added as submodels.

PROTOCOL does not consider processes and properties that more properly relate to the repository than to the waste form. This includes hydrologic flow, prediction of the chemical composition of inflowing ground water, and reactions of dissolved species after they leave the resident water volume, or immediate vicinity of the waste form. However, there is sufficient flexibility in PROTOCOL that such features can be added to the model where sufficient information is available.

7.1.3 Implementation

PROTOCOL is implemented as a set of computer files, FORTRAN-coded logic instructions and data. These files and their use are shown

schematically in Figure 7.1. There is also a supporting set of preprocessor and data files (MANEQL, Figure 7.2) and this set is used independently to maintain the extensive thermochemical data base. Most of the development effort has gone into the PROTOCOL algorithm, whose capabilities and functioning will be described at length in the sections immediately following.

7.1.3.1 Kinetic Capability

At the present state of the art, dissolution models for complex glasses require specific experimental rate data. PROTOCOL makes use of experimental leach rate data in the form of submodels, which can be created and modified as required with relative ease. It is assumed that experimental investigations focused on a single or narrow range of waste form compositions can provide adequate rate functions for component mass fluxes, with linkages to other parameters of the system.

FIGURE 7.2. Preprocessor Files

FIGURE 7.1. PROTOCOL Files

The basic capability installed in PROTOCOL is a menu of polynomial terms with time as the variable, designed to accommodate most empirical dissolution rate expressions. The complete functions are used to generate mass fluxes of species from the solid phase(s). If, as discussed later, more complex relationships are developed, all the values for parameters that they may contain are provided by PROTOCOL, either from its data files and arrays, or by computation.

The kinetic, or solid phase monitoring functions of PROTOCOL were developed from the intuitively attractive concept of the simple rate-to-mass converter (Cheung 1981). In this concept, the concentrations of species in solution change according to experimentally derived functions, possibly approaching a "saturation" concentrations. These functions, which usually include interface area and water volume, entirely define the mass release from a solid.

In its simplest form, the rate-to-mass converter model could not in itself provide an adequate description of a general dissolution system. It did not consider the possibility that the functions might actually contain chemistry-dependent terms that would not transfer to a different system. Although it was recognized that the observed or net rate of a reaction must be some function of the degree of saturation with respect to certain phases, the identities and solubilities of the controlling phases in the system are not generally known. For this reason, coupling of a rate model with a chemical stability model was essential.

7.1.3.2 Equilibrium Capability

It is well known that the dissolution of complex glasses usually leads to the formation of new material at the solid-aqueous interface, with compositions and properties that are different from those of the bulk glass. This may result both from selective leaching of the glass surface and from precipitation from solution. The material can have significant effects (solubility constraints) on the composition of the aqueous phase, which is the main concern of this study.

It has been found that steady states are in fact produced, in which solution compositions are constant. In water flow regions where the concentrations of aqueous species are independent of residence time, as described elsewhere in this report, we may interpret the steady states as equilibria. That is, saturation concentrations are controlled by

the thermodynamic stabilities of solid phases and can be calculated by equilibrium methods.

The thermodynamic capability of PROTOCOL is used to monitor reactions in the aqueous phase, which are assumed to be sufficiently fast that local equilibrium is maintained. This equilibrium section of the model is unaware in a formal sense of any solid phases that it has not precipitated. Their presence is registered only by incrementing component mass arrays. Therefore, reactant phases can be considered that are not thermodynamically stable in water. The activities performed are to redistribute dissolving components, set solubility constraints on dissolution and identify precipitated or converted solid phases. This equilibrium function has been provided by the attachment of a geochemical code, MINEQL (Westall, Zachery and Morel 1976), as sets of subroutines and data files. An extensive thermodynamic data base, and preprocessor and postprocessor have been provided. These features are discussed in Appendix B.

7.1.3.3 System Monitoring

In its role as a system monitor, PROTOCOL couples experimentally derived rate functions with thermodynamic equilibrium calculations where these are appropriate, and with water flow rates. The equilibrium calculation provides data for feedback to stored rate functions that involve water composition, and PROTOCOL computes from them mass fluxes of component species. It also records the redistribution of elements leaving the aqueous phase, whether by precipitation or outflow, and writes a tabular summary of the status of the system with time.

Simulations are carried out in a series of discrete time increments. During each increment, both kinetic and equilibrium computations of reactions leading to mass transfer are made. Each set of computations is repeated at predetermined time intervals to follow the progress of the reactions. The output is a detailed numerical description of the composition of the remaining solid waste form, the composition of the resident water, the identities and masses of precipitates predicted to form, and a summary of the masses of component elements released to the outflowing groundwater as a function of time.

7.1.4 Simulation Modes

There is a considerable variability in experimental conditions and in applications to repository conditions that PROTOCOL might be

required to simulate. In addition to the specific set of system parameters, a variety of options have therefore been developed, which are selected through instruction files. The following outline summarizes the modes in which the program can presently be run, and how the various parameters are used to set up problems.

In all the options a resident water volume is specified. Note that in the modes 1A through 1D, to be described below, the MINEQL input file (PRODT1E) specifies the entire chemistry of the system. This is in contrast to static sequential and flowing systems, where it specifies only the water composition, and leached moles are calculated from rate functions.

In modes 1, 3A and 3B the calculation times are generated as terms in the function:

$$t_n = t_0 f^{n-1}$$

where t_n is an elapsed time in days, t_0 is an arbitrary time of first calculation, f is the time increment factor, and n is the increment number which starts at 1 and increases to a specified limit. There is also a direct control of the maximum simulation time.

7.1.4.1 Mode 1: Static Continuous

The reaction time is not used internally, and any rate constants in the file are ignored. This is a "step zero" calculation: it is not in a time sequence and is an equilibration of material from the MINEQL input file. This includes components initially in the water and whatever is known to have been leached into it. In the following are summarized the various static continuous modes in which PROTOCOL can currently be run. Modes 1A and 1B use experimental measurements directly and assume nothing, while 1C and 1D are more exploratory exercises using external rate functions.

- A. Fully documentable case: The reacted masses of all components are known, including the analytical concentrations of dissolved elements and the masses and elemental compositions of alteration/precipitation phases. If, as is usually the case, the solid phase information required for 1A is not available, the problem can be run in three alternate modes B-D.
- B. A complete set of measured aqueous concentrations is input and the disequilibrium indices of dissolved solid phases in the output file (PROOUT) examined for evidence of approach to saturation. If non-

ideal phases are found experimentally, their stabilities are evaluated from the aqueous activities of their components, either directly or statistically.

- C. A dissolution is assumed that is congruent with respect to some measured element and the "mobilized" concentrations of other elements are precalculated and used as input. Solid phases are identified either as computed precipitates or as non-ideal phases.
- D. Rate functions from closely related experiments are used to precalculate the total moles of components mobilized in the total elapsed time. MINEQL then does a distribution of the total masses in the system, leached plus leachant.

7.1.4.2 Mode 2: Static Sequential

This approach can model either a series of sacrificial duplicates or repeated sampling of a single experiment, assuming negligible perturbation. Although these procedures are similar to the simple leach experiment of mode 1, periodic measurements of the changes in concentrations can be used to derive rate functions.

7.1.4.3 Mode 3: Flowing Water

A time sequence of analyses for a single sample at constant residence time is assumed. The following suboptions are available:

- A. The flow rate is specified as a fixed value.
- B. The flow rate is calculated from a specified linear velocity, a repository configuration and a simple model of water flow.
- C. The flow rate and a set of additional calculation times are specified by a water change schedule. The times and fraction of leachate replaced are listed as input parameters.

7.1.4.4 Mode 4: Steady State

A metastable equilibrium may be reached, in which the activities of aqueous components remain constant within analytical precision. Basically, there are two possibilities: the observed final rate of release of a component is equal either to the gross or net rate of leaching. If the component does not appear in an alteration phase (or if a precipitation rate is negligible), its measured gross rate

equals the true rate of leaching. This could be independent of flow rate in a high flow rate system, but in general would be a function of aqueous composition. With enough experimentation, it should be possible to construct such a true leach rate function containing activity and temperature dependences.

An observed rate would be a net rate where a significant fraction of the mobilized component is incorporated into a solid phase. This would generally result in an increase in mass of phase(s), but that might be obscured if the activity of the component in some phase is also changing.

Some calculations and interpretations are external to the program. One option is to examine the evidence of dissolved solutes by simulating the distribution of elements in an analyzed leachate. Each analysis is run as an equilibration problem. If the data on solid phases were complete and accurate, running a problem in this mode would not compute that significant masses of precipitates should form. Actually, it may be possible to identify a dissolved solid at saturation, or more likely, to deduce the stability of a solid of variable composition that is assumed to be saturated on the evidence of constant stabilized leachate activities (see 7.2.4.1, for example). A detailed mass balance in each determination is precluded without experimental information on the solid phases formed and total moles of components removed by exchange. Of course, a mass balance is not necessary if only release data are required.

The most information can be obtained by reconstructing the system at saturation for a specific run, i.e., determining the solid composition, either by direct analysis or by difference. A difference calculation requires data for the total reacted masses and for the total dissolved masses of components.

7.1.5 Options

7.1.5.1 Congruency

A recurring question in dissolution studies is the extent to which components dissolve congruently. An option has therefore been provided to calculate congruent rates automatically, based on the rate for any component that is selected: all other input rate functions are ignored. This option makes it possible to study the effects of assuming that a constant fraction of the whole waste form reacts at a specified rate. Of course, it cannot require that all elements remain in solution, but allows precipitates to form.

This option corresponds to a reaction progress type of simulation for a closed system, but at a rate based on some observed element. Other related options that could be added are arbitrary constant and arbitrary variable (with time) congruent rates.

7.1.5.2 Species Selection

PROTOCOL selects from the isothermal thermochemical data file all possible species for the problem input. A great many of these are actually superfluous for specific problems, falling into one of two categories: aqueous species at activities many orders of magnitude too small to be significant and dissolved solids that are a like distance from possible precipitation. Such species may be significant in other specialized systems and cannot be rejected until the problem has been run. In PROTOCOL, however, the system simulation is performed many times, offering opportunities of reducing the data base. Both dissolved solids and aqueous complexes are subject to deletion.

7.1.5.2.1 Dissolved Solids Selection Option. Large numbers of potentially precipitating phases are selected in many-component systems of ground water and glass. Enough information is available in increments 0 and 1 to compute a maximum value of each activity product that could be reached in the specified time. Even these very rough criteria are sufficient to allow the deletion of many phases from further consideration. The user specifies only a maximum reaction time: deletion is then automatic.

7.1.5.2.2 Aqueous Complex Selection Option. The number of iterations can be substantially reduced by the deletion of trivial aqueous complexes during a run. Many such species in the data base are of such low relative stability that they cannot possibly be significant (in a specific system). An option is available by which the user can specify some conservative threshold activity: species not meeting this criterion are tagged and not considered further.

7.1.5.3 Water Flow and Change

Two types of simulations for water movement have been provided. In the flow mode, which may be on either an experimental or repository scale, the mass of water is computed from an input volume flow rate. The moles of dissolved components and complexes in this volume increment are added to the arrays for released species and subtracted from the total mass of the system that is available for the next distribution. Similarly, the

moles of components in the inflowing test water or groundwater are added to the inventory of available material.

In some experimental designs sampling is done at scheduled intervals. An option is therefore provided in the model for the exchange of specified fractions of the resident water volume on a schedule listed in the input instruction file. The exchange intervals are, however, independent of the step timer, so that the progress of reactions may be studied between exchanges.

7.1.6 Features

7.1.6.1 Thermodynamics of Surface Products

The solid materials for which published stability data are available in the data bases of PROTOCOL and other general-purpose chemical codes are mostly crystalline phases with well-defined stoichiometries and Gibbs free energies of formation. In the leaching of minerals and glasses at low temperatures, however, both crystalline and amorphous solid products may be formed at the interface, and both may be variable in composition. Although the amorphous materials are thought to be metastable solid solutions, they can persist for long periods of time and appear to interact reversibly with dissolved species. The fact that these apparently metastable equilibrium aqueous concentrations can be attained after extended leaching under static or low flow conditions implies the existence of solubility controls on dissolution or release. This is of sufficient importance that, in addition to a constant aqueous composition, it is also desirable to secure confirmatory thermochemical evidence of the stability of the system. This requires the determination of thermochemical properties of the surface material and their incorporation into the PROTOCOL data base.

In certain simple cases, as in the well-known reactions of the metastable phases of silica, steady states can be treated thermodynamically and the activities of dissolved species reflect the structures of the solids in a predictable way. It is likely that the analysis of reactions forming more complex metastable phases can also be undertaken by thermodynamically-based models, provided that the energies of the bonds that are formed are characteristic of the solid being leached and the temperature, and that the product phases do not undergo further alteration at significant rates.

One approach to the chemical modeling of a disordered phase is to treat it numerically as a mixture of discrete component phases, with individual stabilities. The advantage of this procedure is that each such component phase can be treated in simulation as a dissolved solid with a stability that can be related to an equilibrium aqueous composition.

The methodology of Tardy and Garrels (1974) is a well-known procedure for the estimation of the stabilities of layer silicates that may be applicable to the less ordered products of glass dissolution. They showed that for the layer silicate structure, the component oxides make constant contributions to the total free energy of the phase. It was possible to make estimates of their stabilities that were consistent not only with those of composite phases, but with solubility data, i.e., the activities of dissolved species in equilibrated leachates. The free energies of formation of simple oxides as "silicated" components that were determined in this way are in many cases very different from their standard state values, reflecting their degree of bonding. Once determined, however, they could simply be added and subtracted to construct other complex phases of similar structures but different stoichiometries and previously unknown stabilities.

The concept can be extended to the alteration products of specific glass compositions at constant temperature if there is sufficient regularity in the structures that are formed.

In the present application, we do not exactly duplicate the Tardy-Garrels approach, since there is not a comparable set of alteration product phases known to be of similar structure and with known thermochemical properties. For our purposes, this set must be generated from the reference glass composition.

The most direct approach is to measure experimentally the concentrations of dissolved species. As they approach steady state, the free energies of reaction computed from the activity products also become constant. If the solid composition is also known, the overall reaction can be written, and the value of the composite solid phase free energy computed. It may also be possible to estimate the stabilities for silicated components that are otherwise difficult to determine by constructing plots of free energy of silication versus element electronegativity.

A similar but somewhat less direct approach can be taken if the leaching rates of components are definable by an appropriate set of input functions (submodels). Since PROTOCOL monitors the mass balance in the system, it can record the overall reaction, K_{eq} and ΔG of reaction as a function of time. It must, of course, be told exactly which components and species are to be included.

7.1.6.1.1 Application. Successive equilibria can be simulated with the appropriate rate functions and system parameters, but with a data file which contains a set of silicated components and their saturated log K values. These "dissolved solids" in the MINEQL definition precipitate individually according to their assigned stabilities and the activities of their components in solution.

7.1.6.2 Submodels

Many processes and functional forms have been proposed to interpret the complex dissolution behaviour of glasses. No general-purpose leaching function of wide applicability has been developed, although expressions have been derived for individual components of some glasses that fit experimental data reasonably well.

PROTOCOL was designed to function as a simulator without a commitment to specific rate expressions or leaching mechanisms. The value of this flexibility may be seen in the fresh insight into the complex of leaching processes that has developed in the course of this program.

In order to accommodate the variety of rate functions that are expected to result from intensive investigations of waste glass leaching, they are input to PROTOCOL as submodels. The numerical format has been kept as simple and generic as possible, with a minimal requirement for recoding. The dynamic values for physical parameters and chemical activities that may be required are provided for their evaluation. A distinct advantage of this approach is that no normalization of experimental data is necessary: the transfer of rates to other systems is accomplished by resetting a small number of values for parameters in the instruction and data files.

The first submodel to be created, primarily for development purposes, was for silica, where the reactions are relatively simple and where rate constants for both forward and reverse reactions have been determined. Examples of its use are given in Section 7.2.2.

The second submodel was a general-purpose rate expression, providing a menu of terms whose coefficients can be derived by fitting experimental data (Appendix B.2.4). No mechanistic interpretation of the data is required or implied. These functions are composite in that they are likely to be complex summations of the rates of both forward and (unknown) reverse reactions. In this mode, function fitting of aqueous concentration data is done off-line to produce mass fluxes in terms of cumulative mass transferred per unit area per unit time.

There is another, more sophisticated class of expressions that are being and have been developed by various investigators. In these, the terms in rate functions are associated with specific chemical and physical processes. They also contain constants which are obtained by the investigator by fitting experimental data. Inasmuch as they contain variables other than time, they are implemented individually by adding coding to the subroutine in which mass increments are calculated. The third submodel that has been attached is of this class: it is that proposed by Kuhn for soluble elements in a specific nuclear waste glass composition, and is based on a surface coverage mechanism (Kuhn and Peters 1982).

This mechanistic option has been exercised with estimated constants and appears to be working as designed. Further development and analysis have not been attempted at this time, since its usefulness will depend on the derivation of constants (or functions) for other waste glass components and compositions. Rate functions which include dependences on the chemical activities of dissolved and sorbed species are, however, the most promising approach to the development of generally useful glass leaching kinetic models.

7.1.7 Program Size and Timing

7.1.7.1 Program Size

Two FORTRAN versions of PROTOCOL are maintained, for the CDC-7600 and the CRAY-1. The lengths are about 4,600 and 5,100 lines, respectively, and they are dimensioned for 49,000 words. The CRAY-1 version contains an additional set of subroutines for online graphics.

The size is greatly dependent on the intended use. It has been configured for present purposes to treat large and chemically complex systems. It currently accommodates a maximum of 2 waste form phases with 26 components per

phase, 12 precipitated phases, 140 components in the basis set, 30 silicated component phases, and 600 total species. It should be noted that of the 140 basis species, only 75 have actually been assigned.

7.1.7.2 Timing

Run time is dependent on the following variables; number and types of components in the system, size of the isothermal data file, number of time steps, quality of starting estimates, and volume of output requested. As a rough guide, it has been found that a typical system of 17 basis set components with a thermochemical file of maximum size (298K and common elements) and normal output files but without large excursions in redox ratios, will require about 13 seconds for the initial equilibration (step 0) on the CRAY-1 and 5 seconds for each succeeding step.

7.2 ILLUSTRATIONS AND APPLICATIONS

7.2.1 Simple Dissolution: Silica

For the present purpose, a simple dissolution process is characterized as that in which a

single component is removed from a solid into pure, neutral, static, air-saturated water at 298K, where the only variables are the interfacial area and the water volume. One of the simplest examples relating to glass-water reactions is the free dissolution of a stable or metastable form of silica. It is known that the various forms of silica have characteristic leach rates which are largely a function of their crystallinity (Rimstidt and Barnes 1980).

In this simplest case, there are no concentration effects to restrict dissolution, i.e., no significant buildup of silica in solution. This would be approximated in the earliest part of a leaching experiment. In a flowing system it would also be approached at a high flow rate, and at elevated temperatures in a Soxhlet extraction. The result is a constant rate of release, as shown in Figure 7.3 for an interfacial area of one square meter.

In systems where the aqueous species leached are not removed, the reverse reaction will become significant, as also shown in Figure 7.3. The solution concentration increases with time to saturation at a rate

FIGURE 7.3. Dissolution Rates for Amorphous Silica at 298K

resulting from the summing of forward and reverse reactions. Simulation now requires rate constants for the two reactions, or for the net reaction. In addition, the reverse reaction is concentration dependent, so that the extent of the system, A/V, must also be known. This introduces the resident water volume as a new parameter.

In the development of PROTOCOL, a series of exercises was carried out to examine and verify its operation, using tabulated rate functions for silica. The purpose of these simulations was to assure the correct functioning with respect to the effects on release of solubility, water composition, temperature, water volume, flow rate, ratio of interfacial area to water volume, and the accuracy of thermochemical data.

Recognizing the sluggish kinetics of crystallization of silica at low temperatures, the crystalline forms were removed from the active segment of the data file, and are to be replaced only for systems where they are specifically recognized to appear.

Variations were run on a leaching problem, in which 10 grams of amorphous silica were dissolved into 100 mL of neutral water. Some

results of these computations are shown in Figures 7.4 through 7.8. Note that concentrations in the resident water volume have been plotted, not the total mass of silica lost by leaching. Values for parameters were varied in the following ranges:

- Temperature, 313K-363K. Rates increase appropriately with increasing temperature, and precipitation and constant molality are achieved at correspondingly earlier times (Figure 7.4).
- Water flow rate, 0-1 mL/day. Minor effects of flow rate on the concentration in solution of H_4SiO_4 were found. Changes in molality as a function of time and flow rate are plotted in Figure 7.5.
- Interface area. The effects are shown of varying this parameter between 10^{-1} and $10^1 m^2 g^{-1}$ (Figure 7.6).
- Initial concentration of silica, 10^{-4} to 10^{-20} molal. (Figure 7.7). The inhibiting effect of an initial concentration in the water of the species being leached is shown clearly. It is also clear that in an experimental context, the magnitude of the effect would depend very strongly on

FIGURE 7.4. Computed Aqueous Silica Concentrations as a Function of Temperature. Amorphous silica in contact with static water at pH = 6.

FIGURE 7.5. Computed Changes in Dissolved Silica Concentrations as a Function of Flow Rate. Amorphous silica at 313K and pH = 6.

FIGURE 7.6. Computed Effects of Surface Area on Dissolved Silica Concentrations. Amorphous silica in static water at 313K and pH = 6.

FIGURE 7.7. Computed Effect of Initial Silica Concentration on Dissolved Concentrations. Amorphous silica in static water at 313K and pH = 6.

FIGURE 7.8. Computed Effects of Changes in Stability of H_4SiO_4 on Time to Saturate. Amorphous silica in static water at 313K and pH = 6.

when measurements were taken. (In some situations, the progress of reactions can be predicted in simulation that would not be within experimental precision.

Sensitivity to thermochemical stability data. The $\Delta G_{f, 313K}^0$ for H_4SiO_4 has been used as a variable (Figure 7.8), not because of actual uncertainty in this value, but to simulate a reaction in which the stability of a species that might be formed is not well known.

7.2.2 Nonstoichiometric Phases

The estimation of the standard free energy of formation of montmorillonite at 298K that was made by Tardy and Garrels (1974) was used to explore a possible application of code calculations to nonstoichiometric phases. Their list of silicated components was used as a data file for dissolved solids in PROTOCOL simulations. Their estimated free energies of formation were used in the usual way to calculate values for log K in the formation reaction from the MINEQL basis set components.

The result of this calculation was that the contributing "phases" of montmorillonite, Fe_2O_3 , Al_2O_3 and SiO_2 precipitated, but

$Mg(OH)_2$ did not. The solubilities of these elements did not match those determined experimentally (Weaver, Jackson and Syers 1971). The next step was to reverse the calculation, and use PROTOCOL to determine the free energies of formation of the silicated components that were required to produce the observed solubilities reported by Weaver.

The result of these calculations are shown in Table 7.1. For example, if we consider the "phase" SiO_2 (silicated), its solubility at 298K can be computed as a function of an assigned free energy of formation. The actual quantity varied is log K for the solid phase formation reaction written in the MINEQL convention:

A sufficient mass of the component species $SiO_2(OH)_2^{2-}$ specified in the problem to ensure precipitation. The repetitive capability of PROTOCOL allows the calculation to be done any required number of times, generating the function shown in Figure 7.9.

TABLE 7.1. Estimated Stabilities of Montmorillonite

Silicated component	Moles	$\Delta G_{f, 298K}^0$ kJ/mole (Tardy and Garrels)	$\Sigma \Delta G^0$	$\Delta G_{f, 298K}^0$ kJ/mole (PROTOCOL)	$\Sigma \Delta G^0$
$Mg(OH)_2$	0.29	-851	-247	-898	-261
SiO_2	3.81	-856	-3261	-862	-3284
Al_2O_3	0.86	-1600	-1376	-1562	-1343
Fe_2O_3	0.11	-743	-82	-758	-84
H_2O_{exc}	0.20	-245	-49	-245	-49
H_2O_{sil}	0.71	-248	-176	-248	-176
			-5191		-5196

* (ΔG_f^0 from solubility (Tardy and Garrels) = -5194 kJ/mole)

FIGURE 7.9. Solubility of Silica at 298K as a Silicated Component Versus Assigned log K for Reaction 1

The solubility given by Weaver, Jackson and Syers (1971) is $10^{-3.1}$ M at 298K. From Figure 7.9, this corresponds to a log K for reaction (7.1) of 26.13 and to a ΔG° of -38.16 kJ/mole. From this we calculate $\Delta G^\circ_{f,298}$ for $\text{SiO}_2(\text{sol})$ of -861.9 kJ/mole.

The calculations could in principle be done by hand, but speciation must be considered, and a code calculation is more efficient. The distribution of silica species in this relatively simple case was 1.3% H_4SiO_4 , 48.2% H_2SiO_3 and 50.5% $\text{H}_2\text{Si}(\text{OH})_6$. It is apparently not possible to determine the properties of the two types of ground water in this way. The values of free energies and therefore contributions of the various components are different from those of Tardy and Garrels, but the stability value for montmorillonite obtained by summing them is the same. This apparently reflects the difference in speciation between the model and that assumed by Tardy. The conclusion at this time is that both methods give the correct result, providing they are used consistently, and that the procedure can be used to determine the relations between thermochemical properties and composition, both of the solid and aqueous phases.

7.2.3 Multicomponent Materials

Dissolution is considerably complicated by the participation of more than one chemical component, from either the glass or the aqueous solution. Historically, it has not been possible to extrapolate experimental rate functions very far in time or to use them to quantitatively predict behavior in different reaction systems. The reason is that such functions are likely to contain system-specific values for some parameters, which may not be obvious. For example, reaction rates usually contain terms involving the activities of dissolved species, which become significant at some point in the leaching process. These in turn may be affected by other reactions that are in progress. Many leaching reactions are sequential and cannot be predicted directly from early experimental observations.

Although we can identify most of the parameters that modify leach rates, the actual forms of the leaching functions are generally complex. Most important are increases in activities leading to saturation with respect to new phases. Discontinuities in leaching rates at phase changes are reflected in such

phenomena as "solubility limits" where total concentrations of some components begin to be controlled by interactions with a new solid phase. The time of appearance and composition of a new phase may, however, be difficult to identify experimentally.

Solids that can release multiple components also allow incongruent dissolution, and the new phases that are formed can depend on the ratios of these release rates. That is, although quasi-equilibrium states can be identified, they are profoundly affected by rate processes, and the entire history of the system.

In general, rates of dissolution depend on two interrelated factors: detachment and transport. Detachment rates depend on the difference in activity between solid and solution. They may, therefore, be modified by any process that changes the distribution of the components in the system, including transport. Transport can be by flow, convection and diffusion in the solution, or by diffusion in the solid.

7.2.3.1 SRL Glasses

As discussed in Section 7.1.4, several options are available for the analysis of leaching processes. Flowing systems are of the greatest interest with respect to the estimation of radionuclide release, and much of the data developed in this program is of this type. Inasmuch as it has been found that flow experiments can be run to apparent steady states, data are commonly reported as final aqueous compositions rather than as rate functions.

If steady states are indeed reached and can be confirmed as basic properties of the glass, extrapolation to repository conditions can reasonably be carried out. A very important consideration in this respect is to examine the evidence for residual phase stability.

Because of the disordered state of the interfacial material that is formed, the use of conventional data for solid phases is precluded. The alternative is to assume that metastable equilibria have been established, and to develop specialized stability data for alteration products by the methodology outlined in 7.2.2.

If the residual material is thermochemically metastable, it will react to mass transfer or pH change by a change in the molar ratios of its components in the solid but not in the

aqueous phase. Those components should maintain constant values of free energy of formation over some solid compositional range, which in turn determines the activities of their aqueous species.

PROTOCOL was used as a stability calculator to examine these relationships. All dissolved solids in the data file were removed, except for a brief list of silicated component phases. Reverse solubility calculations were carried out as discussed in Section 7.2.2. The full isothermal file for aqueous complexes was used, and the speciation for the various elements was determined.

The first data examined were those of Table 1.3.1 for TDS-131 glass. These were steady state aqueous compositions determined at 343K (70°C). The resulting free energies of formation for the silicated component phases are shown in Table 7.2 and Figures 7.10 through 7.21.

Inspection of Table 7.2 reveals some interesting features of the alteration products of this glass. First, since the oxides involved show stability differences of only 4-15 kJ/mole between 298K and 343K, it was thought acceptable to include some of the Tardy-Garrels data for montmorillonite at 298K for comparative purposes.

By comparison to the Tardy-Garrels data for phyllosilicates, it appears that the residual material more closely resembles a proto-clay than an assembly of oxides. The trend of free energy values is equally interesting. There is a distinct correlation for alkali and alkaline earth components with pH. Since the H^+ activity enters into the free energy calculations, these values should not correlate with pH. We must conclude that they are not strongly bonded components of the surface phase, although the number and self-consistency of the steady-state determinations shows that they have predictable solubilities as a function of pH.

Note that alumina and the major component oxides of silicon and boron do not show these trends. The bonding of boron in the solid is established immediately at a lower value, and does not change. Silica also attains a constant stability value which is very close to that of quartz. Although no quartz has been observed in these experiments, the values can hardly be coincidental. Much the same behavior was noted by Tardy and Garrels: the silication energy for silica is very low and it reacts much like a pure phase.

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Section 1.1.1.1

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FIGURE 7.10. Estimated Stabilities of Alkali and Alkaline-Earth Components Versus pH

FIGURE 7.11. Estimated Stability of Component Silica

FIGURE 7.12. Estimated Stability of Component B_2O_3

FIGURE 7.13. Estimated Stability of Component Al_2O_3

FIGURE 7.14. Estimated Stabilities of Alkali and Alkaline-Earth Components Versus S/V

FIGURE 7.15. Estimated Stability of Component Silica Versus S/V

FIGURE 7.16. Estimated Stability of Component B_2O_3 Versus S/V

FIGURE 7.17. Estimated Stability of Component Al_2O_3 Versus S/V

FIGURE 7.18. Estimated Stabilities of Alkali and Alkaline-Earth Components Versus Residence Time

FIGURE 7.19. Estimated Stability of Component Silica Versus Residence Time

FIGURE 7.20. Estimated Stability of Component B_2O_3 Versus Residence Time

FIGURE 7.21. Estimated Stability of Component Al_2O_3 Versus Residence Time

Chapter 1. The results of the stability estimates for the oxide components of the interfacial material that have been derived from steady-state aqueous compositions are given in Tables 7.3 through 7.8.

The relationships are entirely consistent with those found for the SRL-131 waste glass composition. This is illustrated by the data of Tables 1.10 and 7.3 for the defense waste reference glass, which have also been plotted in Figures 7.22 through 7.33. Estimated stabilities of the alkali and alkaline earth components are again seen to be functions of pH in the range 9-10.5 (Figure 7.22). The

data for different residence times have been plotted together, and are indistinguishable. Figures 7.23 through 7.27 show the estimates for SiO_2 , B_2O_3 , Al_2O_3 , Fe_2O_3 and UO_3 , respectively. These five components show no significant dependences on pH, S/V or residence time.

The data of Tables 1.11 and 7.4 have been plotted in Figures 7.28 through 7.33. The data include experiments with deionized water, ground water and iron, and have been plotted together. It is evident that although the scatter is greater than for the series with deionized water alone, the

TABLE 7.3. Estimated Free Energies of Formation for Oxide Components^(a) of Leached Residues from DWRG Glass, kJ/mole. Concentration data from Table 1.10, deionized water leachate.

T	S/V	Tres	pH	Si	B	Al	Na	Ca	Sr	Cs	Li	Fe	U
373.	10.	4.	9.04	-866	-1279.	-1683.	-694.	-695.	-708.	-762.	-755.	-661.	-1121.
373.	81.	4.	9.67	-861.	-1274.	-1681.	-674.	-685.	-698.	-743.	-736.	-665.	-1117.
373.	88.	4.	9.84	-861.	-1276.	-1685.	-671.	-684.	-697.	-740.	-732.	-665.	-1118.
373.	157.	4.	9.46	-861.	-1273.	-1679.	-679.	-689.	-702.	-746.	-739.	-662.	-1118.
373.	266.	4.	9.87	-860.	-1274.	-1681.	-668.	-683.	-696.	-738.	-729.	-662.	-1115.
373.	291.	4.	9.77	-861.	-1275.	-1682.	-672.	-684.	-697.	-741.	-733.	-662.	-1115.
373.	970.	4.	9.83	-860.	-1274.	-1681.	-669.	-683.	-696.	-740.	-730.	-661.	-1115.
373.	1940.	4.	9.91	-860.	-1274.	-1682.	-667.	-682.	-695.	-738.	-728.	-660.	-1114.
373.	10.	28.	9.05	-862.	-1272.	-1679.	-688.	-691.	-704.	-758.	-748.	-661.	-1119.
373.	81.	28.	9.70	-860.	-1273.	-1682.	-673.	-683.	-697.	-743.	-732.	-664.	-1116.
373.	88.	28.	10.39	-860.	-1279.	-1692.	-660.	-677.	-690.	-733.	-719.	-673.	-1113.
373.	157.	28.	9.58	-859.	-1271.	-1679.	-673.	-685.	-691.	-747.	-729.	-655.	-1115.
373.	266.	28.	10.00	-859.	-1273.	-1682.	-666.	-679.	-692.	-738.	-725.	-662.	-1114.
373.	291.	28.	10.01	-859.	-1274.	-1682.	-666.	-679.	-692.	-738.	-725.	-663.	-1114.
373.	970.	28.	10.26	-858.	-1274.	-1685.	-659.	-677.	-690.	-734.	-718.	-669.	-1113.
373.	1940.	28.	10.34	-858.	-1274.	-1686.	-656.	-676.	-688.	-733.	-716.	-673.	-1112.

(a) Oxides assumed were SiO_2 , B_2O_3 , Al_2O_3 , Na_2O , CaO , SrO , Cs_2O , Li_2O , Fe_2O_3 and UO_3

TABLE 7.4. Estimated Free Energies of Formation for Oxide Components^(a) of Leached Residues from DWRG Glass, kJ/mole. Concentration data from Table 1.11, including effects of ground water and ductile iron.

T	S/V	Tres	pH	Si	B	Al	Ca	Sr	Cs	Li	Fe	U
373.		4.	9.71	-859.	-1309.	-1705.	-676.					
373.	10.	4.	9.04	-866	-1279.	-1683.	-695.	-708.	-762.	-755.	-661.	-1121.
373.	10.	4.	9.58	-859.	-1291.	-1693.	-677.	-700.	-761.	-754.	-692.	-1119.
373.	10.	4.	9.89	-861.	-1290.	-1699.	-676.	-697.	-749.	-745.	-644.	-1118.
373.	91.	4.	9.67	-859.	-1281.	-1684.	-677.	-694.	-741.	-741.	-660.	-1115.
373.	81.	4.	9.67	-861.	-1274.	-1681.	-685.	-698.	-743.	-736.	-665.	-1117.
373.	88.	4.	9.84	-861.	-1276.	-1685.	-684.	-697.	-740.	-732.	-665.	-1118.
373.	92.	4.	10.38	-860.	-1281.	-1692.	-669.	-684.	-722.	-723.	-653.	-1115.
373.	266.	4.	9.87	-860.	-1274.	-1681.	-683.	-696.	-738.	-729.	-662.	-1115.
373.	224.	3.	9.69	-859.	-1279.	-1684.	-676.	-694.	-738.	-738.	-660.	-1115.
373.	10.	28.	9.05	-862.	-1272.	-1679.	-691.	-704.	-758.	-748.	-661.	-1119.
373.	10.	28.	9.40	-859.	-1284.	-1687.	-680.	-701.	-753.	-751.	-672.	-1118.
373.	10.	28.	10.64	-864.	-1290.	-1702.	-669.	-685.	-724.	-723.	-664.	-1116.
373.	81.	28.	9.70	-860.	-1273.	-1682.	-683.	-697.	-743.	-732.	-664.	-1116.
373.	88.	28.	10.39	-860.	-1279.	-1692.	-677.	-690.	-733.	-719.	-673.	-1113.
373.	91.	28.	9.50	-859.	-1279.	-1685.	-679.	-697.	-745.	-744.	-677.	-1117.
373.	92.	28.	11.30	-863.	-1288.	-1701.	-659.	-672.	-706.	-702.	-664.	-1110.
373.	266.	28.	10.00	-859.	-1273.	-1682.	-679.	-692.	-738.	-725.	-662.	-1114.
373.	224.	28.	9.55	-858.	-1275.	-1684.	-679.	-695.	-740.	-739.	-674.	-1116.

(a) Oxides assumed were SiO_2 , B_2O_3 , Al_2O_3 , Na_2O , CaO , SrO , Cs_2O , Li_2O , Fe_2O_3 and UO_3

TABLE 7.5. Estimated Free Energies of Formation for Oxide Components^(a) of Leached Residues from DWRG Glass, kJ/mole. Concentration data from Table 1.12.

T	S/V	Tres	pH	Si	B	Al	Ca	Sr	Cs	Li	Fe	U
373.		4.	9.71	-859.	-1309.	-1705.	-676.					
343.	304.	4.	9.69	-857.	-1271.	-1642.	-678.	-698.	-748.	-743.	-650.	-1114.
373.	266.	4.	9.87	-860.	-1274.	-1681.	-683.	-696.	-738.	-729.	-662.	-1115.
343.	268.	4.	9.61	-857.	-1286.	-1646.	-676.	-698.	-748.	-744.	-645.	-1115.
343.	224.	4.	9.69	-859.	-1279.	-1684.	-675.	-693.	-738.	-738.	-660.	-1115.
343.	304.	28.	9.83	-858.	-1274.	-1632.	-681.	-694.	-732.	-729.	-628.	-1113.
373.	266.	28.	10.00	-859.	-1273.	-1682.	-679.	-692.	-738.	-725.	-662.	-1114.
343.	268.	28.	9.47	-857.	-1269.	-1641.	-678.	-698.	-749.	-745.	-649.	-1115.
373.	224.	28.	9.55	-858.	-1275.	-1684.	-679.	-695.	-740.	-739.	-674.	-1116.

(a) Oxides assumed were SiO₂, B₂O₃, Al₂O₃, Na₂O, CaO, SrO, Cs₂O, Li₂O, Fe₂O₃ and UO₃

TABLE 7.6. Estimated Free Energies of Formation for Oxide Components^(a) of Leached Residues from PNL 76-68 Glass, kJ/mole. Concentration data from Table 1.19.

T	S/V	Tres	pH	Si	B	Na	Sr	Cs
343.	24.	2.	9.10	-863.	-1276.	-687.	-705.	-757.
343.	24.	8.	9.30	-859.	-1270.	-677.	-704.	-745.
373.	825.	2.	9.60	-859.	-1264.	-664.	-704.	-739.
343.	825.	8.	9.80	-859.	-1262.	-657.	-701.	-734.
343.	825.	28.	9.90	-854.	-1262.	-655.	-700.	-733.

(a) Oxides assumed were SiO₂, B₂O₃, Al₂O₃, Na₂O, CaO, SrO, Cs₂O, Li₂O, Fe₂O₃ and UO₃

TABLE 7.7. Estimated Free Energies of Formation for Oxide Components^(a) of Leached Residues from PGM Glass, kJ/mole. Concentration data from Table 1.20.

T	S/V	Tres	pH	Si	B	Al	Na	Ca	Sr
343.	24.	28.	6.90	-867.	-1267.	-1617.	-735.	-730.	-739.
343.	825.	28.	7.30	-862.	-1260.	-1612.	-722.	-723.	-731.

(a) Oxides assumed were SiO₂, B₂O₃, Al₂O₃, Na₂O, CaO, SrO, Cs₂O, Li₂O, Fe₂O₃ and UO₃

TABLE 7.8. Estimated Free Energies of Formation for Oxide Components^(a) of Leached Residues from DWRG and CUBS Glasses, kJ/mole. Concentration data from Table 1.21.

T	S/V	Tres	pH	Si	B	Al	Na	Ca	Sr	Cs	Li	Fe	U	Ti	Mn
343.	194.	28.	9.81	-859.	-1275.	-1634.	-671.	-683.	-696.	-732.	-731.	-634.	-1113.	-1096.	-364. (DWRG)
343.	194.	28.	8.61	-860.	-1270.	-1621.	-698.	-699.	-711.	-753.	-750.	-631.	-1121.	-1105.	-379. (CUBS)
343.	194.	112.	9.85	-857.	-1273.	-1633.	-668.	-682.	-695.	-732.	-729.	-635.	-1113.	-1097.	-364. (DWRG)
343.	194.	112.	9.85	-857.	-1273.	-1633.	-668.	-682.	-695.	-732.	-729.	-635.	-1113.	-1097.	-364. (CUBS)

(a) Oxides assumed were SiO₂, B₂O₃, Al₂O₃, Na₂O, CaO, SrO, Cs₂O, Li₂O, Fe₂O₃ and UO₃

FIGURE 7.22. Estimated Free Energies of Formation for Oxide Components of Leached Residues from DWRG Glass, kJ/mole. Deionized water leachant at 373K; data from Table 1.10.

FIGURE 7.23. Estimated Free Energies of Formation for Silica in Leached Residues from DWRG Glass, kJ/mole. Deionized water leachant at 373K; data from Table 1.10.

FIGURE 7.24. Estimated Free Energies of Formation for Boron Oxide in Leached Residues from DWRG Glass, kJ/mole. Deionized water leachant at 373K; data from Table 1.10.

FIGURE 7.25. Estimated Free Energies of Formation for Alumina in Leached Residues from DWRG Glass, kJ/mole. Deionized water leachant at 373K; data from Table 1.10.

FIGURE 7.26. Estimated Free Energies of Formation for Iron Oxide in Leached Residues from DWRG Glass, kJ/mole. Deionized water leachant at 373K; data from Table 1.10.

FIGURE 7.27. Estimated Free Energies of Formation for Uranium Oxide in Leached Residues from DWRG Glass, kJ/mole. Deionized water leachant at 373K; data from Table 1.10.

FIGURE 7.28. Estimated Free Energies of Formation for Oxide Components of Leached Residues from DWRG Glass, kJ/mole. Deionized and ground water leachant at 373K; data from Table 1.11.

FIGURE 7.29. Estimated Free Energies of Formation for Silica in Leached Residues from DWRG Glass, kJ/mole. Deionized and ground water leachant at 373K; data from Table 1.11.

FIGURE 7.30. Estimated Free Energies of Formation for Boron Oxide in Leached Residues from DWRG Glass, kJ/mole. Deionized and ground water leachants at 373K; data from Table 1.11.

FIGURE 7.31. Estimated Free Energies of Formation for Alumina in Leached Residues from DWRG Glass, kJ/mole. Deionized and ground water leachants at 373K; data from Table 1.11.

FIGURE 7.32. Estimated Free Energies of Formation for Iron Oxide in Leached Residues from DWRG Glass, kJ/mole. Deionized and ground water leachants at 373K; data from Table 1.11.

FIGURE 7.33. Estimated Free Energies of Formation for Uranium Oxide in Leached Residues from DWRG Glass, kJ/mole. Deionized and ground water leachants at 373K; data from Table 1.11.

results and conclusions to be drawn from them are quite similar to those for the TDS-131 composition.

A fairly consistent picture of the chemistry of leached residues has emerged. Although the initial rates of dissolution of components may be erratic and dependent on the physical condition of the surface, the evidence is that an interface/water system is achieved which exhibits metastable equilibrium behavior, and can be modeled by a thermodynamic approach. Elements other than alkalis and alkaline earths have the most predictable stabilities in the amorphous surface phases formed from specific glasses. Under static conditions or low rates of water flow, they appear to control the concentrations of dissolved species at saturation levels. The concentrations of alkali and alkaline earth species depend on the pH level attained, but the dependence is rather weak and can evidently be derived experimentally.

A set of log K values that has been determined for the silicated oxide components can be resubmitted as a data file for release calculations. They precipitate in the normal way, and generate the appropriate steady-state concentrations of dissolved species.

In the simulation of saturation-controlled systems, no leaching rates are involved, and releases will be linear in time. It is suggested that the solid phase is invariant in the sense that it is composed of a set of silicated oxide components with fixed stabilities, although their mole ratios are likely to be variable. The effects of solid state ordering reactions on solubilities have not been specifically investigated experimentally, but it may be presumed that they will act to reduce the free energies of the solid components, and therefore the saturation concentrations.

The main factors that affect releases in such a system are the volume flow rate of water and the actual stability values. Given values for these variables, longer term releases can be estimated. As an example, the stabilities of Table 7.6 for 373K and pH = 9.69 were selected as a typical set, with a value for Na from Table 7.3 at pH = 9.67. A PROTOCOL exercise was run using a (completely arbitrary) rate of 10 mL/day. The resulting functions are shown in Figures 7.34 and 7.35. Again, although such functions can be conveniently extended linearly in time or flow rate, they probably represent unattainable maximum releases. At 373K, reactions forming

FIGURE 7.34. Estimated Steady-State Releases of Species from DWRG Surface Phase. Flow = 10 mL/day, T = 373K.

FIGURE 7.35. Estimated Steady-State Releases of Species from DWRG Surface Phase. Flow = 10 mL/day, T = 373K.

more stable suites of crystalline solid phases are observed to take place at relatively fast rates, as described in Chapter 2 of this report.

7.3. RECOMMENDATIONS FOR FURTHER DEVELOPMENT

PROTOCOL is a novel and pragmatic approach to the long-standing problem of numerical modeling of the dissolution of complex glasses. It provides a rational chemical basis for the interpretation and extrapolation of experimental data. Three general areas can be identified where improvements and extensions can increase its effectiveness: data base, functions and submodels.

7.3.1 Data Base

7.3.1.1 Thermochemical Properties

The usefulness of data bases for chemical models, including PROTOCOL/MINEQL, is determined by the number, accuracy and self-consistency of entries in their thermochemical data files. The file for 298K is reasonably complete in terms of the species of major components (Appendix B.3). The data for elevated temperatures is still somewhat sparse, and extension in this direction

should be an ongoing activity. The PROTOCOL master file is a new assembly, with information taken from many sources. It is likely that considerable improvement will be realized when a critical review can be made. Because of its size, such a review is a formidable task.

7.3.1.2 Alteration (Surface Gel) Phases

The dissolution rates and dissolved concentrations of several elements including Si, Ca, Al and Fe, seem to be controlled by their partial molal thermochemical properties in material deposited at the interface. The composition and properties of these deposits deserve continued detailed examination, and it is likely that much additional relevant information will be found in the literature.

7.3.1.3 Redox Reactions

Currently all redox reactions in a system are controlled by specifying a single value for the component pE. In view of the known importance of the rates of such reactions, this is not considered a realistic approach. An alternative would be to specify, in the instruction file, ratios of reduced to oxidizing species, and not require an

equilibration. Another might be to allow equilibration only for those components where it has been found empirically to be rapid.

7.3.2 Functions

PROTOCOL is a complex assembly of functional units, some of which have received greater emphasis than others. In the following are suggested some areas where modifications can usefully be made.

7.3.2.1 Activity Coefficients

The computation of activity coefficients in MINEQL requires a value for ionic strength, which changes with each increment. In the existing version, this value is input from an instruction file, but it should be calculated automatically and repeatedly. This can be done after the equilibrium concentrations of the dissolved species are known, which implies an iterative process. In the present application, at long reaction times where the concentrations are not changing rapidly, it will probably be adequate to use for each time step a value calculated in the previous step. These modifications are thought to be a relatively minor task.

MINEQL uses the Davies equation to compute activity coefficients in dilute solutions. It cannot provide reasonable estimates for the ground waters that must be expected in a salt repository.

7.3.2.2 Kinetic Data File, PRODT2K

This file was organized in a simple, linear format. It may become inconvenient for multiphase systems, or for much larger numbers of components. It can be considerably compressed by single line entries for the constants in the rate functions.

7.3.2.3 Function Fitting

The original intent was that all experimental data was to be fit with empirical functions. This is done off-line, and is a time-consuming and somewhat subjective process. When this approach is used, an improvement could be made by using one of the available automatic curve fitting algorithms.

7.3.2.4 Increment Step Size

The current time step size function is described in 7.1.4. It may be desirable to increase the resolution automatically in the vicinity of precipitation or dissolution. The substitution of alternative functions

in subroutine TIME is a relatively minor modification.

7.3.2.5 pH

In MINEQL, the basis species set is entirely arbitrary, and as the components are used to form other species, the reactions are balanced with H^+ and water. Therefore, it is normally advisable to fix the equilibrium H^+ activity, to correspond to a measured value. This precludes the monitoring of pH changes due to the dissolution of material from the glass, a use not envisioned in the writing of MINEQL. It is, however, possible to modify the coding to allow this function.

7.3.2.6 Optimization

Essentially all the development effort for PROTOCOL has gone into its logical functions and data base. Size and speed have not been considered except in the context of machine capabilities. Optimization should produce substantial improvements in efficiency.

7.3.2.7 Convergence

The attached version of MINEQL suffers from occasional convergence difficulties, especially when a problem is not defined carefully. There are several techniques available to correct these occurrences in the future, which can and should be added to PROTOCOL.

7.3.2.8 Auxiliary Basis Set and Switching

As outlined in Appendix B, a prototype switching feature exists in the preprocessor. This should be developed further for a full set of auxiliary components and transferred to PROTOCOL as an automatic feature, to be activated as required during simulation.

7.3.2.9 File Consolidation

The component data file should be transferred from the preprocessor into the master and isothermal data files as a segment of type 1 species. This will require modifications of both PROTOCOL and MINEQL.

7.3.3 Submodels

PROTOCOL does not attempt to explain or predict processes on a molecular scale. It is assumed that they are most reasonably described by experimentally-based dissolution rate functions. It is doubtful that any function, however complex, can be found for

any element that is valid for all glasses dissolving in water of arbitrary composition. Furthermore, the level of insight that is possible is unclear. Nevertheless, several areas can be listed where advances are to be expected.

7.3.3.1 Diffusion

Many attempts have been made to create numerical dissolution rate models based on the diffusion of species through near-surface material. It does not now appear that any of these expressions are useful in the general case. PROTOCOL is designed to allow them to be inserted and evaluated for specific systems, and a great deal of evaluation of such functions remains to be done. A relatively simple submodel for solid state transport is possible where there are not strong interactions between migrating species and host matrix. However, heavy metals do not move freely between phases.

7.3.3.2 Congruency

It is most likely that dissolution rate data for some soluble, congruently dissolving elements from borosilicate waste glasses can be fit by existing models.

7.3.3.3 Ordering

No attempt has been made in this program to account for the effects of rates of ordering reactions in the surface material. Depending on the temperature, however, these may have important effects on aqueous composition and release.

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APPENDIX A
REFERENCE MATERIALS

APPENDIX A

Reference Materials

Two reference materials were provided to participants in the Leaching Mechanisms Program for use in their investigations. One material was a reference defense waste glass of a prototypical borosilicate composition containing uranium. Portions of this glass were later doped with technetium at Pennsylvania State University, and with neptunium and plutonium at the Pacific Northwest Laboratory, for special investigations conducted at those two laboratories. The second reference material provided to each of the participants was a prototypical mild steel such as might be used for fabrication of an overpack container in a geologic repository.

This appendix describes the two reference materials.

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APPENDIX A

REFERENCE MATERIAL

In order to promote uniformity in the co-operative Leaching Mechanisms Program, two reference materials were furnished to all of the participants, a defense waste reference glass (usually referred to as DWRG in this document) and a mild steel. In addition, when the participants used a synthetic ground water in their tests, they were requested to use the basalt ground water formation described by Jones (1982).

This appendix describes the manufacture and analysis of the DWRG and the analysis of the mild steel. Note that those reference materials were not available until about a year into the program. Thus, this document contains considerable data obtained with another, now obsolete, defense waste glass formulation, SRL TDS-131 (see Table 1.1, Chapter 1), which was available to all of the participants at the outset of the program.

A.1 DEFENSE WASTE REFERENCE GLASS

A.1.1 Fabrication

This glass was produced at Savannah River Laboratory. After melting at SRL, it had been poured into stainless steel cans and cooled. It was received in this form by the MCC in 1982. A total of 16 cans were received, containing approximately 15 kg of glass.

At MCC the glass was chipped out of the cans and crushed to a particle size of -8 Tyler mesh. All of the crushed material was combined in a large container and stirred to ensure homogeneity. The mixed crushed glass was remelted, 450 g/melt, in a platinum crucible. Each melt was held at 1150°C for 30 minutes and then poured into bar molds of 1.9 x 1.9 x 17.8 cm. Two bars were produced from each melt, each weighting approximately 220 g. In all, 65 bars were produced. As soon as a cast bar had cooled to the point where it was structurally stable (5-10 seconds), it was removed from the mold and placed in an annealing furnace where it was held at 550°C for 2 hours. After annealing, the bar was furnace cooled to 100°C at a rate

of 40 to 50°C per hour. The bar was then removed from the furnace and cooled to room temperature. The finished bars were numbered 1-65 on both ends and a 2 cm archive segment sawn from one end of each.

A.1.2 Characterization

A.1.2.1 Characterization Methodology

Analyses were conducted on twelve samples obtained from 9 different randomly chosen archive bar-segments. These were sampled at two locations; 1 sample was obtained from each of the remaining 6 segments. These samples were crushed to -100 Tyler mesh particle size, fused and put into solution for ICP and fluorometric uranium analysis. Four additional samples for X-ray diffraction (XRD) analyses and scanning electron microscopy (SEM) were obtained from three of the archive segments used for compositional analysis. The XRD samples were not crushed prior to analysis. Fracture surfaces were used for the SEM examination.

A.1.2.2 Results

The composition of SRL reference glass is shown in Table A.1. Homogeneity of the glass was satisfactory. Relative standard deviation (RSD) for concentrations of all except 3 constituents was better than 5%, and for all major components the RSD was less than 1%. The sum of concentrations of all constituents (expressed as the % of all oxides assumed to be present) was 100.12%.

No crystallinity was found in three of the XRD samples. An amount near the detection limit (3-5%) was found in the fourth sample. Two peaks were seen. The stronger could have been due to UO_2 crystals, but positive identification was not possible due to its low magnitude. The weaker peak was not identifiable.

The SEM examination revealed nearly featureless conchoidal fracture surfaces. Five small (5-10 μ m diameter) bubbles were seen in a 5500 μ m by 4000 μ m area of one sample.

TABLE A.1. Composition of Defense Waste Reference Glass, wt%

Oxide	Average Concentration	Standard Deviation	Relative Standard Deviation, %
Al ₂ O ₃	6.69	0.04	0.6
B ₂ O ₃	6.63	0.03	0.5
CaO	1.97	0.02	1.0
Ce ₂ O ₃	<0.1		
Cr ₂ O ₃	<0.02		
Cs ₂ O ₃	0.33	0.01	3.0
Fe ₂ O ₃	10.40	0.08	0.8
K ₂ O	0.44	0.10	22.7
La ₂ O ₃	<0.02		
Li ₂ O	4.94	0.04	0.8
MgO	0.88	0.03	3.4
MnO ₂	2.17	0.10	4.6
MoO ₃	<0.02		
Na ₂ O	9.04	0.05	0.6
Nd ₂ O ₃	<0.1		
NiO	1.90	0.02	1.1
P ₂ O ₅	<0.2		
S	<0.2		
SiO ₂	50.32	0.24	0.5
SrO	0.48	0.00	0.3
TiO ₂	0.10	0.01	10.0
U ₃ O ₈	3.01	0.08	2.7
ZrO ₂	0.82	0.24	29.3
Total	100.12		

A.1.2.3 Conclusions

The SRL reference glass is a compositionally uniform glass with no significant crystallinity, voids or other nonglassy phases present. It is suitable for use as a reference material.

A.2 REFERENCE MILD STEEL

The reference mild steel used in the Leaching Mechanisms Program was AISI 1020 steel, in the form of 1/16-in. hot-rolled sheet from Pittsburgh Steel Heat No. B27625. Analysis are given in Table A.2.

As shown in Table A.2, the material had a decarburized surface layer which was found to be 63 μ m deep. The bulk analysis was provided by the vendor; the surface analysis was done by the MCC.

TABLE A.2 Analysis of Reference Mild Steel

Element	Bulk, wt%	Decarburized Surface, wt%	
C	0.19	0.01	0.02
Mn	0.36	0.28	0.27
P	0.29	0.006	0.010
Si	0.43	0.01	0.016
Fe	Remainder	Remainder	Remainder

A.3 REFERENCE

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APPENDIX B
USE OF PROTOCOL

APPENDIX B

Use of PROTOCOL

Additional details on the use and operation of PROTOCOL, which supplement the information in Chapter 7, are given in this appendix.

APPENDIX B Use of PROTOCOL

Additional details on the use and operation of PROTOCOL, which supplement the information in Chapter 2, are given in the appendix.

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APPENDIX B

INSTRUCTIONS ON USAGE OF PROTOCOL

B.1 USAGE OUTLINE

The input for PROTOCOL is from a set of problem files. Files are most conveniently prepared by modifying existing files with a text editor. The usual procedure for running PROTOCOL can be summarized as follows:

1. Generate a rate function from experimental data, using terms from the existing menu. If this is not possible, a new submodel can readily be created by additional coding.
2. Set up the kinetic file (PRODT2K), using the rate constants and waste form data.
3. Create a run instruction file (PRODT1K).
4. Create an aqueous phase composition file for MINEQL (PRODT1E).
5. Use the preprocessor MANEQL if an update in the thermochemical file (PRODT2E) for the experimental temperature is required.
6. Assemble the set of files and run the compiled version of PROTOCOL (PROCON).

On initialization, PROTOCOL reads the kinetic file, computes waste form physical parameters, the resident water volume and flow rate. It then enters a nest of three loops in time, phase and component, where it remains until completion of the problem.

In each element of the time loop a step length is computed and a water equilibration is carried out. In each element of the phase loop are performed calculations for its individual components; rate functions and resulting mass fluxes and geometric changes. Finally, compositional changes due to water mixing and flow are determined and entries made in the output tables, completing the time step.

B.2 FILES

Aside from specific instructions that direct the computations, the information in the data

base is organized on four levels. These pertain to the experimental or repository system, to the waste form, to the chemical phases in that waste form, and to the individual component elements in each phase. In outline form, the following information is required:

SYSTEM:

- A. Temperature
- B. Water
 1. Volume flow rate
 2. Resident volume or film thickness
 3. Density
 4. Initial chemical composition

WASTE FORM:

- A. Mass, surface area, density, physical dimensions
- B. Number of component phases

PHASE:

- A. Mass and density
- B. Number of components

COMPONENT:

- A. Mass and density
- B. Formula weight and charge
- C. Leach rate data
- D. Thermochemical properties and formation reactions of species in other phases

B.2.1 Thermochemical Instruction File

The thermochemical instruction file (PRODT1E) is a slightly modified version of the MINEQL input component data set. It is a table of components in the system, listed by type

(B.2.5.1). A value for the total or analytical concentration of each component is required, and a guess as to its final concentration at equilibrium. For each element that has a variable oxidation state, a redox couple must be available in the data base, and both members must be specified as components. In PROTOCOL/MINEQL, H^+ and e^- are also components, must be specified, and are used to fix the pH and pE, respectively.

The listing for PROTOCOL is more extensive, since it must contain not only those components initially in the water, but those that are to be leached from the solid. Although concentrations for the latter must be specified, they are set at negligible values.

B.2.2 Kinetic Instruction File

This file (PRODT1K) provides most of the specifications of the physical system for the simulation, as well as time step and print instructions. The principal options available are:

WASTE FORM:

Geometry - cylindrical or irregular

Interfacial area

Initial mass

TIME STEP:

Initial step size

Increment factor

Maximum number of steps

Simulation time limit

WATER:

Flow or static

Volume

Density

Flow rate

PRINT:

Option for table of identification and stabilities of species considered

B.2.3 Thermochemical Data File

The publicly available MINEQL data file contains component identification numbers,

stoichiometric coefficients and logarithms of the equilibrium constants for reactions. These reactions are for the formation of species from a set of basis species, or components at 298K. Their origins are unspecified.

Changes in component species have been made to reflect the present application to inorganic materials. Organic ligands have been removed and many actinide components have been added. The current components are listed in Table B.1. Missing numbers have not been assigned (or reassigned). Some components are available that are not required for the specific application to waste glass/repository/ground water systems.

TABLE B.1. Revised Listing of MINEQL Components

1. Ca^{2+}	27. Sn^{4+}	54. $TcOOH^+$
2. Mg^{2+}	28. La^{3+}	55. Fm^{3+}
3. Sr^{2+}	29. Ce^{3+}	56. Ti^{3+}
4. K^+	30. Au^+	58. Ra^{2+}
5. Na^+	31. Th^{4+}	101. CO_3^{2-}
6. Fe^{3+}	32. UO_2^{2+}	102. SO_4^{2-}
7. Fe^{2+}	33. Cu^+	103. Cl^-
8. Mn^{2+}	34. U^{4+}	104. F^-
9. Cu^{2+}	35. $Zr(OH)_5^-$	105. Br^-
10. Ba^{2+}	36. Pu^{3+}	106. I^-
11. Cd^{2+}	37. Pu^{4+}	108. S^{2-}
12. Zn^{2+}	38. PuO_2^+	109. PO_4^{3-}
13. Ni^{2+}	39. PuO_2^{2+}	110. $P_2O_7^{4-}$
14. Hg^{2+}	40. Np^{3+}	111. $P_3O_{10}^{5-}$
15. Pb^{2+}	41. Np^{4+}	112. $SiO_2(OH)_2^{2-}$
16. Co^{2+}	42. NpO_2^+	118. $B(OH)_4^-$
17. Co^{3+}	43. NpO_2^{2+}	122. MoO_4^{2-}
18. Ag^+	44. Tc^{4+}	123. WO_4^{2-}
19. Cr^{3+}	46. Am^{3+}	124. AsO_4^{3-}
20. Al^{3+}	47. Am^{4+}	125. HVO_4^{2-}
21. Cs^+	48. AmO_2^+	127. NO_3^-
22. Li^+	49. AmO_2^{2+}	135. IO_3^-
23. Be^{2+}	50. H^+	136. TcO_4^-
24. Sc^{3+}	51. Cm^{3+}	
25. $Ti(OH)_4^0$	52. Bk^{3+}	
26. Sn^{2+}	53. Cf^{3+}	

The thermodynamic data file that has been used in this project is an extended version under development at Lawrence Livermore National Laboratory. In addition to increases in the numbers of components and other species, it contains for each species S^0 , ΔH^0 of formation, ΔG^0 of formation, a literature reference number, chemical formula, and mineral name, if any.

The master file was created by extending the file for 298K linearly to accommodate data for elevated temperatures: each entry for a species is followed by similar line entries for higher temperatures. Data at any temperature can be accepted, and thermochemical properties can be entered in either kcal or kJ. A pointer is provided for the conversion of units. This master file is revised on a continuous basis. It presently contains 878 dissolved solids and 922 aqueous species.

B.2.4 Kinetic Data File

The kinetic data input file (PRODT2K) has three levels of data, in which are specified properties of a waste form, phase and chemical component. To accommodate complex waste forms, it can be extended linearly to any length consistent with the dimensions of the current arrays.

The waste form is characterized by an identification number, overall density, length/radius ratio (if cylindrical), and number of phases. Each phase has an identification number, initial mass and density, and number of components. Each component has an identification number, density, mass fraction of its phase, submodel pointer, and a set of eight constants.

The interpretation of the constants depends on the submodel that has been selected. If submodel 1 is used, for example, a wide variety of rate functions can be constructed by summing from a menu of terms in powers of time that is provided. If other terms are required, they can be added with minor coding modifications. If dependences on parameters other than time are available, other submodels are easily added by redefinition of the input constants.

A modification of input rate functions has been found useful for components of an element in different oxidation states. Very large changes in the ratios of such components may take place during iteration, depending on the specified oxidation potential. Considerable iteration time can often be saved by assigning oxidation state ratios for an element according to those determined

in the previous increment, no matter what the input rate functions may be.

B.2.5 Output Files

For each problem that is run, PROTOCOL writes summary tables, recording its instructions and data base, as well as the status of the waste form as a function of time. Complex changes in the distribution of elements must be monitored. The composition of the resident aqueous phase is continuously modified by leaching from the waste form, by precipitation and dissolution, and by water flow. The species involved in these processes may be multicomponent.

An accounting system ensures that all the data on these mass transfer processes are retrieved and tabulated. The distributions are recorded in terms of the list of chemical components (basis species) defined in Table B.1. The masses and concentrations of components, aqueous complexes and precipitated solids are stored in "attribute" arrays, which classify them as inflowing, leached, resident or released by outflow. In addition, separate arrays record the identification numbers, stoichiometric coefficients, and concentrations of the components of multicomponent species. As species are gained or lost in each time step by reaction and flow, all the appropriate arrays are debited or credited.

Output files were created for these detailed distributions to ensure that mass balance is maintained and documented under all circumstances.

B.2.5.1 Detailed Equilibration Data

The normal output of MINEQL is a detailed summary of the activities at equilibrium of all species that were considered in the problem (Westall, Zachary and Morel 1976). In MINEQL, all chemical species are assigned to one of six types, summarized briefly as follows:

1. Components - basis set of soluble species, from which species of all other types are formed
2. Complexes - all other soluble species
3. Species at - gases at fixed partial
fixed pressure, precipitated
activity solids not allowed to dissolve, fixed pH or Eh, and redox reactions
4. Precipitated solids subject to dissolution

5. Dissolved solids subject to precipitation
6. Species not to be considered, usually for kinetic reasons.

The format of this main output file has been retained with little change as a description of intermediate states in the dynamic leaching process: one such tabulation can be generated for each time step. However, because of the large volume of output, an option has been made available to limit it to the first three steps. The output parameters in this tabulation are the component concentration C , $\log C$, $\log K$ for species formation, and the species formula expressed as sets of component identification number and stoichiometric coefficient.

B.2.5.2 Run Instructions, Kinetic Data and Waste Form Status Summary

The output file PROSUMW contains 5 tables. Output tables 1 and 2 are verbatim records of instruction file PRODT1K (B.2.2) and kinetic data file PRODT2K (B.2.4), respectively. A summary of output data relating primarily to the waste form is written into output table 3. Values are tabulated in each time step for the following parameters for all components in each leached solid phase:

- Increment number
- Reaction time
- Phase and component identification numbers
- Mass corrosion rate
- Cumulative fraction mobilized
- Mass mobilized
- Cumulative mass remaining
- Cumulative depth depleted
- Cumulative water volume flowed.

An annotation is also made in each time step of precipitated phases, including temporary and permanent identification numbers, chemical formula, and mineral name, if any. (Output tables 6 and 7 are described in B.2.5.5.)

B.2.5.3 Component Distribution and Release

The main summary output file is output table 4 (file PROSUMC). It records the distribution in time of all material in the system (external to the waste form), as well as

all that has entered by water inflow and left by outflow. In each time step, a single line entry is written for each (MINEQL) component listing current values for the following parameters:

- Cumulative moles leached
- Resident plus cumulative moles added from inflowing water
- Initial (start of increment) cumulative moles lost to outflow
- Cumulative moles available for distribution
- Molality of distributed (uncomplexed) component
- Molality of distributed complex
- Total molality of component in complexes
- Molality of component in precipitated phase (individual and total)
- Current moles lost to outflow
- Final (end of increment) cumulative moles lost to outflow
- Cumulative fraction of component released.

The actual activities of aqueous complexes in most time steps are normally of no interest. Since they require a large amount of print-out space and are also available elsewhere (B.2.5.1), their inclusion in output table 4 has been made optional. For comparative purposes, entries are also included for the masses of precipitated phases, expressed as molalities.

B.2.5.4 Deleted Species

A tabulation is made (output file PRODEL) of all species that have been rejected (7.1.5.2) in time steps 0 and 1. In this table are listed for each species the identification number, molality if aqueous, QMAX and QMAX/KEQ if a dissolved solid.

B.2.5.5 Species Identification and Stabilities

In the interests of quality assurance and of clarifying PROTOCOL, a self-referencing capability has been provided. An option is available which attaches to a simulation a record of the value and origin of every datum that was used. The tabulation is necessary

because the data files are subject to frequent revision as described in section B.3 and because PROTOCOL selects for each problem a potentially unique set of input data. The intent is to provide enough information with the problem output that a meaningful independent evaluation or recalculation could be carried out. Two documentation output tables 6 and 7 can be automatically generated for every run, and are printed in output file PROSUMW.

Output table 6 lists species that were selected from the isothermal data file and considered in the computation. For each species are tabulated its chemical formula, serial number, standard free energy of formation, mineral name (if any), and reference number.

Output table 7 is a list of references for the free energy values, or for the information that was used to derive them. A listing of free energies is more meaningful than log K values for this purpose, since the latter refer to reactions written according to a specific set of rules and using a specific basis component species set (Table B.1). These reactions are not stored in a readily retrievable form, and the basis set is itself subject to modification.

B.2.5.6 Terminal Output

PROTOCOL is designed to be run in a time-sharing mode from a remote terminal. During simulation, the operations are directed by files, and interaction with the user takes place only if the online graphic option is exercised (B.2.5.7). Output to the terminal is a report of the course of the computations, and consists of the following information:

- Increment number and seconds of computer time used at the end of each increment
- Precipitation and dissolution of phases, reported by phase identification number
- MINEQL standard error messages
- PROTOCOL error messages, and MINEQL supplementary error messages, often including diagnostics or references to probable source locations in the coding
- Increment number and reason for termination if normal exit (such as exceeding allowed simulation time or number of increments)

- Summary of computer time used if normal exit, including central processor, system and input/output times.

B.2.5.7 Graphics

Two types of graphics capabilities are available. The first is an online plotting option using GRAFLIB, a graphics library written in LRLTRAN (LLNL FORTRAN) for use on the Livermore Timesharing System. Versions exist for the CDC-7600, CRAY-1 and VAX machines. A package of 5 subroutines in PROTOCOL is used to plot data as they are generated during the simulation. The following operations are performed:

- A plot option is requested (time function of component molalities, component molalities in complexes, component percent distribution in species, component mass in precipitates, or component release)
- The available components are listed, and the selection of a set of 4 is requested
- A standard grid is drawn, labeled and titled
- A key is written, associating plot symbols with components
- Data are plotted as soon as they are calculated
- Precipitated phases are listed by identification number in a separate key as they are formed.

A postprocessor is also provided to plot data from the output files; it was used to draw the figures for Chapter 7. For portability, this program uses the widely available CRAY-1 DISPLA 9.0 graphics library: it can be used on machines with 4, 5, 6, 8 or 10-character words. POSTP is file oriented to keep recomputations to a minimum. This is implemented by generalized coding, keeping all the instructions and data in an external file, which is essentially a string of macros, one for each plot. Each instruction value is identified with its variable name and a brief description of its purpose. Numerical data are in a simple array of 12E10.3 values.

The site-dependent linkages have been grouped in a block of coding for easy replacement when necessary. The following features are currently available and can be requested by text editing of the input file.

- Arbitrary plot size and orientation
- Specifiable title, frame, grid, axes, labels, ticks and connecting lines
- Automatic legend write
- Fourteen character styles, some with shading options
- Nineteen symbol options
- Segmenting of curves for arrays with zero values
- Multiple plots from each table
- Multiple curves on each plot
- Unlimited number of input tables
- Completely arbitrary selection of ordinate and abscissa
- Sorting option, puts abscissa values in monotonically increasing order.

B.3 PREPROCESSOR

The thermochemical data base (MASTER file) that has been developed for PROTOCOL is maintained by a preprocessor program (MANEQL, MANager for EQUilibration data). This is necessary because of the number of species in the file and the additional entries for elevated temperatures (1800 species, 5000 total entries).

The preprocessor has two files, a brief instruction file and a data file. The data file contains literature references and values of standard free energy of formation for the set of basis species (components) at 298K and at 50K intervals from 323K to 723K. Nearly all the data at 623K and above are estimates, with high uncertainties. The instruction file contains a list of options for processing data files. These options control master file revision, isothermal file generation and basis species switching.

B.3.1 Preprocessor Features and Options

B.3.1.1 Master Thermochemical File Revision

The preprocessor revises the master thermochemical file as required by changes in the data. It computes equilibrium constant values for every species in the file with a value for its free energy of formation. The revised entry is written into a storage file (NEWMAS). An instruction directs the pro-

gram to either retain the temporary species identification numbers or to renumber. If renumbering is to be done, another instruction specifies the interval between successive numbers.

The data changes that are processed are of three types: standard free energy of formation of a component, standard free energy of formation of another type of species and a value for log K for the species formation reaction. A change in standard free energy of formation for a component will be propagated throughout the data file, changing values for a large number of species in which it appears. A change of standard free energy of formation of a species will be reflected in a single change in its value for log K. Interpolations are carried out as required to obtain the necessary values from the component data file. If a log K value is changed and no free energy value is listed, the latter will be calculated and written in the appropriate field in the storage file.

If the user does not wish to write out the species formation reaction, an option is available for interactive data input, with semiautomatic balancing. If the first component field for an entry is empty, MANEQL prompts for 4 components, bound H and O in the species, and water of hydration.

In each case where a significant change in a log K value has been made, the old entry is rewritten and is followed by the new entry, identified by an asterisk in column 1 of the data line. The purpose of this is to allow the user to see exactly what changes in data have resulted, and their magnitude.

A scan is made of the new data storage file to count the numbers of species of the five types. During this scan, if only a single entry for 298.1K for a species is listed, a Van't Hoff estimate for 373K will be attempted to provide data for the temperature region 298.1K to 373K. Finally, data from the storage file are rewritten into a new MASTER file with their appropriate type segment headings.

B.3.1.2 Isothermal File Generation

This option is called with a Kelvin temperature specification: ready-to-use isothermal data files are generated in a two step process for any temperature to the nearest 0.1K from 298.1K to 700K. MANEQL reads the master file and, wherever the data permit, writes entries into a new isothermal file for the requested temperature. This is done either by selecting the appropriate entry from

MASTER, or by interpolating between free energy of formation values for higher and lower temperatures.

After completion of this process, a scan is made of the new data file, counting the numbers of species of types 2-6. These sums and the segments containing the 5 species types are then written into a final revised file. No data revisions or species renumbering are carried out in the generation of isothermal files.

B.3.1.3 Basis Species Switching

In most cases, the original MINEQL basis species were the simplest aqueous ions of the elements. It often happens, and especially with cations, that these are not the major species and are occasionally reduced in concentrations enough to cause difficulties in convergence. The problem can often be resolved by switching to a major species as the basis for the computation. However, manual switching for a large data base is prohibitive in terms of the time and effort required. The alternative is to designate a set of auxiliary basis species and create the required logic to exchange them as required.

The status of this feature for PROTOCOL is that the switching has been set up as an option in MINEQL, exercised by setting a flag in the instruction file and specifying the

identification number of the species to be switched. A subroutine is called which makes the required changes in log K values, component identification numbers, stoichiometric coefficients, free energy values, reference numbers, and chemical formulas.

The feature is a prototype in the sense that it is at this point able to do the switch for a single component at 298K, that is, from the basis species Fe^{3+} to FeOH^{2+} . Most of the logic for other component changes is in place, and this feature will be developed further. The option has been tested and it generates a new isothermal data file with all the necessary data changes correctly made.

The result is that basis set revisions are now feasible in terms of time and effort. There are other components for which the option will be very useful, such as uranium and silicon. The silicon basis is $\text{SiO}_2(\text{OH})_2^{2-}$, which should for most purposes be converted to H_4SiO_4^0 .

B.4 REFERENCE

Westall, J., J. Zachary and F. Morel. 1976. MINEQL: A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems. Technical Note No. 18, Massachusetts Institute of Technology, Cambridge, Massachusetts.

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APPENDIX C

LEACHING MECHANISMS IN POLYPHASE CERAMIC HIGH- LEVEL NUCLEAR WASTE FORMS

APPENDIX C

Leaching Mechanisms in Polyphase Ceramic High-Level Nuclear Waste Forms

When initiated, the Leaching Mechanisms Program was designed to study the leaching of both glass and crystalline waste forms. At about one year into the program, when the decision was made officially that the DWPF waste form would be glass, the sponsor requested that the Leaching Mechanisms Program concentrate solely on glass. At that time the investigations at Rockwell International Science Center and Pennsylvania State University, the two laboratories in the Program who had been given basic responsibility for investigating the leaching of crystalline waste forms, were reoriented to emphasize glass. This Appendix summarizes the results of the investigations into the leaching of crystalline waste forms obtained prior to reorientation of the Program.

The studies at Rockwell International Science Center emphasized the leaching of polyphase ceramics, the studies at Pennsylvania State University emphasized single phase dissolution. These studies conclusively showed that the ceramic leaching mechanisms were phase specific, with the behavior of the individual phases being similar to the pure phase analogs. The crystalline reaction products were observed in the studies indicating that for the more soluble phases in the ceramic form, solubility ultimately becomes the factor controlling the leach rate in a constrained flow system. This was not conclusively shown for the more stable crystalline phases, which, though not in equilibrium with an aqueous environment, react so slowly that their dissolution may be considered to be under kinetic control.

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APPENDIX C

LEACHING MECHANISMS IN POLYPHASE CERAMIC HIGH-LEVEL NUCLEAR WASTE FORMS

C.1 CHEMICAL AND PHASE COMPOSITION OF CERAMIC WASTE FORMS

Polyphase ceramic nuclear waste forms were selected as the alternative to borosilicate glass for the consolidation of high-level defense wastes by the National Alternative Waste Form (AWF) Program in 1982 (DOE 1980; Bernadzikowski et al. 1983). The ceramic forms under consideration at that time were assemblages of crystalline phases designed to chemically bind the elements present in Savannah River Plant (SRP) wastes in stable host lattice sites. These ceramic assemblages were formulated through the use of chemical additives with the waste and controlled redox calcining of both waste and additives before consolidation at temperatures between 1000 and 1200°C under pressures of 2,000 to 10,000 psi. The reference defense waste used in these studies differed from that used in the borosilicate glass development efforts in that the Al in the waste was not removed for volume reduction. The composition of the SRP composite waste without Al removal is given in Table C.1 (Bernadzikowski et al. 1983).

The two most promising ceramic types developed during the AWF Program were a form based on the use of titania, silica, calcia, and zirconia additives (labeled SYNROC-D) and another using alumina, silica, and zirconia with the waste. Both ceramic forms shared common phases and processing steps, had waste loadings of 60 wt%, and densities near 4 g/cm³. The titania-containing ceramics have been the most extensively studied and will be used as the basis for this summary. However, the more simple alumina-silica based assemblage will also be considered comparatively in the development of the mechanistic description of ceramic waste form dissolution behavior.

The alumina-silica based ceramics consisted of a five-phase assemblage of magnetoplumbite, nepheline, spinel, uraninite, and corundum. Alumina, silica, and zirconia must be added to the waste to adjust its chemical composition to produce this form. The formu-

TABLE C.1. Nominal Savannah River Plant "Composite, Without Al Removal" Simulated High-Level Waste Composition. Variations of 10 to 15% in major component concentrations between studies exist because of updates in the SRP waste compositions between 1979-1983. Radionuclide simulant concentrations and minor components used in any given study were highly variable (Bernadzikowski et al. 1983; Morgan et al. 1981; Jantzen et al. 1981; Harker et al. 1982a; Morgan and Cirilin 1982; Ryerson, Burr and Rozsa 1981; Campbell et al. 1982; Harker et al. 1982b; Morgan et al. 1984).

Component Oxide	Weight %	Minor Elements Added In Specific Studies	
Fe ₂ O ₃	31.4	Na ₂ SO ₄	PbO
Al ₂ O ₃	30.4	Na ₃ PO ₄	Ce ₂ O ₃ ^(a)
MnO ₂	7.1	MgO	PrO ₂ ^(a)
U ₃ O ₈ ^(a)	4.4	Cr ₂ O ₃	Nd ₂ O ₃ ^(a)
CaO	4.2	CuO	ThO ₂ ^(a)
NiO	2.2	ZnO	
Na ₂ O	5.1	SrO ^(a)	
SiO ₂	8.2	Cs ₂ O ^(a)	
HgO	2.2	BaO	
Zeolite ^(b)	5.1	La ₂ O ₃ ^(a)	

(a) Radionuclide simulants.

(b) Approximate composition 54% SiO₂, 19% H₂O, 16% Al₂O₃, 5% Na₂O, 3% Fe₂O₃, 2% CaO, and 1% MgO.

lation, phase content, and elemental distribution of the ceramic, labeled CSRL-60, are given in Table C.2 (Morgan et al. 1981; Jantzen et al. 1981; Harker et al. 1982a). In processing, the waste was reduced by controlled calcination to the point that the uranium in the consolidated ceramic appeared in the 4+ state. This also reduced a fraction (up to 30%) of the Fe in the waste to 2+. The U and Zr formed a fluorite

TABLE C.2. Formulation and Composition of CSRL-6U, Alumina-Silica-Based Polyphase Ceramic for SRP High-Level Waste Immobilization (Harker et al. 1982a)

Formulation:

Final Density: 3.7 to 3.9 g/cm³

Composite SRP waste - 60.0 wt%
 Al_2O_3 - 35.8
 SiO_2 - 4.0
 ZrO_2 - 0.2

Processing Conditions: Hot isostatic pressing 1040°C, 10,000 psi

Calculated Volumetric Phase Content:

Magnetoplumbite - 33 vol%
 Nepheline-Glass - 30
 Spinel solid solution - 24
 Corundum - 12
 Uraninite solid solution - 1

Elemental Distribution:

Phase	Nominal Stoichiometry	Elemental Content
Magnetoplumbite	$X^{2+}Y_{12}^{3+}O_{19}$	X = Sr, Ca, alkali _{0.5} + Rare Earth _{0.5} Y = Al, Fe (+minor Al, Mn, Si)
Nepheline	$NaAlSiO_4$	Na, Al, Si, Cs, Ca, trace Fe
Spinel	$X^{2+}Y_2^{3+}O_4$	X = Fe, Mn, Ni Y = Al, Fe
Corundum	Al_2O_3	Al, Fe
Uraninite	UO_2/ZrO_2	U, Zr, Th, 4+ actinides
Amorphous material		Na, Si, Al, Ca, Fe, Mn, Ni, Cs

structure solid solution as UO_2/ZrO_2 while the Al^{3+} and Fe^{3+} in the waste formed the magnetoplumbite phase, $(Sr,Ca)(Al,Fe)_{12}O_{19}$ with the larger divalents and charged balanced combinations of trivalents and monovalents. The remaining Fe was incorporated, along with nickel and Mn in a hercynite-type spinel ($FeAl_2O_4$), and the alkali reacted with silica and alumina to form nepheline ($NaAlSiO_4$) and a continuous amorphous intergranular phase. Any residual Al produced corundum, Al_2O_3 . The radionuclide hosts in the simulated waste ceramic are well defined. Uraninite hosts the 4+ U and Th, magnetoplumbite the Sr and rare earths, while Cs is incorporated in the nepheline and glass phases. The distribution of other radionuclides can be predicted from crystal chemistry and natural analogues (Morgan et al. 1981, Morgan and Cirlin 1982).

The SYNROC-0 type ceramics (requiring titania, calcia, zirconia, and silica as additives to the waste) also used nepheline as

the designed host for alkali, but used zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$) as the primary actinide hosts. It was found, however, that the final phase composition of the titania ceramics had a significant dependence upon the oxygen fugacity present in the consolidation process. When the U is present as 4+ and the bulk of the Fe exists as 2+, an assemblage is produced which has been labeled Lawrence Livermore National Laboratory version LLNL-S29 (Ryerson, Burr and Rozsa 1981; Campbell et al. 1982). This ceramic has a number of crystalline phases, as shown in Table C.3, and a significant amount of intergranular amorphous material. The actinide host phases effectively take up uranium and rare earths in this composition and nepheline hosts Cs, but Sr tends to concentrate in the amorphous material (Harker et al. 1982b).

A modified version of the titania-silica ceramic (labeled RSC-S29) was developed at the Rockwell International Science Center in

TABLE C.3. Formulation and Composition of LLNL SYNROC-D S-29 Type Titanate Polyphase Ceramic for Immobilizing SRP Composite Simulated High-Level Waste (Campbell et al. 1982)

Formulation:

Final Density: 3.9 to 4.0 g/cm³

Composite waste - 62.7 wt%
 TiO₂ - 18.8
 SiO₂ - 6.6
 ZrO₂ - 6.6
 CaO - 5.3

Processing Conditions: Reduce Fe to 2+, hot press 1050 to 1200°C, 2000 to 4000 psi.

Calculated Volumetric Phase Content:

Spinel (ulvo and hercynite types) - 40 vol%
 Nepheline + amorphous phase - 27
 Zirconolite - 18
 Perovskite - 15

Trace phases: magnetoplumbite, murataite-type cubic phase, alpha and gamma iron alloy (Harker et al. 1982b)

Elemental Distribution:

Phase	Nominal Stoichiometry	Elemental Content
Hercynite-type spinel	FeAl ₂ O ₄	Al, Fe, Mn, Ti, trace Ni, Ca
Ulvo-type spinel	Fe ₂ TiO ₄	Fe, Ti, Mn, Al, Ca, trace Ni
Nepheline	NaAlSi ₃ O ₈	Al, Si, Na, K, Ca, Fe, Cs
Zirconolite	CaZrTi ₂ O ₇	Zr, Ti, Ca, U, Fe, Mn, trace Al, Si
Perovskite	CaTiO ₃	Ti, Ca, U, Zr, Sr, Na, Al, Ce, Nd
Amorphous phase		Si, Al, Fe, Ti, Ca, Mn, Na, Sr, Cs
<u>Trace Phases</u>		
Magnetoplumbite	CaAl ₁₂ O ₁₉	Al, Fe, Ti, Mn, Ca, Si, Na, Ni
Murataite-type cubic phase	Zr(Ca,Mn) ₂ (Fe,Al) ₄ Ti ₃ O ₁₆	Ti, Fe, Zr, Al, Mn, Ca, Ce, Nd, U, Si, Na, Ni
Alpha and gamma Fe alloy		Fe

which minimal reduction was applied to the waste to keep the Fe as 3+ (Harker et al. 1982b; Morgan et al. 1984; Ryerson 1984). Uranium was found to completely reduce to 4+ in the final ceramic after being fired to 800°C in argon, because of the high free energy of crystallization associated with the formation of zirconolite. The large amount of trivalents in the waste and additives produced the desired Sr host, magnetoplumbite (Morgan and Cirlin 1982), upon consolidation, with the remaining Fe³⁺ forming spinel ((Ni, Mn, Fe)Fe₂O₄) and pseudobrookite (Fe₂TiO₅) as

shown in Table C.4. The actinide host zirconolite was still present as well as a new actinide host murataite, nominally Zr(Ca,Mn)₂(Fe,Al)₄Ti₃O₁₆ (Morgan and Ryerson 1982). Several trace phases are also present, hematite (Fe₂O₃), corundum (Al₂O₃), and an undesirable haüyne-type phase (Ca₂Na₆Al₆Si₆O₂₄(SO₄)₂) formed in reaction of the nepheline with residual sulfate not removed during calcination.

In addition to the changes in the crystal chemistry between the two titanate ceramics,

TABLE C.4. Formulation and Composition of the Rockwell International Science Center RSC-S29 SYNROC-D Type Ceramic for Immobilizing SRP Simulated Composite High-Level Waste

Formulation:

Final Density: 3.9 to 4.0 g/cm³

Composite SRP waste - 62.7 wt%
 TiO₂ - 18.8
 SiO₂ - 6.6
 CaO - 6.6
 ZrO₂ - 5.3

Processing Conditions: Fire waste and additives at 750 to 850°C in inert gas, HIP at 1040°C, and 5000 psi.

Estimated Volumetric Phase Content:

Nepheline - 27 vol%
 Zirconolite - 20
 Murataite-type cubic phase - 20
 Spinel (magnetite-type) - 13
 Magnetoplumbite - 12
 Perovskite - 8
 Amorphous trace

Elemental Distribution:

Phase	Nominal Stoichiometry	Elemental Content
Nepheline	NaAlSiO ₄	Si, Al, Na, K, Ti, Cs
Spinel (magnetite-type)	Fe ₃ O ₄	Fe, Ti, Mn, Al, trace Ca, Ni
Zirconolite	CaZrTi ₂ O ₇	Zr, Ti, Ca, U, Fe, Mn, Al, Th
Perovskite	CaTiO ₃	Ti, Ca, Fe, Mn, Zr, U, Sr, Si, Al, Na, rare earths
Murataite-type cubic phase	Zr(Ca,Mn) ₂ (Fe,Al) ₄ Ti ₃ O ₁₆	Ti, Fe, Zr, Al, Mn, Ca, Ce, Nd, U, Si, Na, Ni
Magnetoplumbite	(Ca,Sr)(Al,Fe) ₁₂ O ₁₉	Fe, Al, Ti, Mn, Ca, Sr, Si, Na, Ni

Trace Phases

Amorphous material		Si, Al, Na, Ca, Fe, Ti
Pseudobrookite	Fe ₂ TiO ₅	
Hematite	Fe ₂ O ₃	
Hauyne (impurity in nepheline)	Ca ₂ Na ₆ Al ₆ Si ₆ O ₂₄ (SO ₄) ₂	
Corundum	Al ₂ O ₃	

brought about by redox control differences, there are distinct differences in composition of the nepheline and glass phases. The LLNL-S29 material shows a distinct separation of the nepheline and glass, with the glass phase surrounding the individual pockets of nepheline. The hot isostatically pressed

(HIPed) RSC-S29 material shows little or no separate glass phase with a less well defined nepheline stoichiometry. This is seen in the EDXS spectra in Figure C.1, in which the LLNL-S29 (version LS04) nepheline grains show a pure NaAlSiO₄ stoichiometry, while the RSC-S29 material contains significant Ca, Fe,

FIGURE C.1. Energy Dispersive X-Ray Analysis of Individual Grains of Nepheline ($\text{NaAlSi}_3\text{O}_8$) in the Two SYNROC-D Type Ceramics. The RSC-S29 ceramic nepheline grains show the presence of Fe, Ca, Ti, and trace K. The LLNL-S29 (version LS04) (b) has a very pure nepheline, containing stoichiometric amounts of Na, Al, and Si.

and Ti. These elements, along with Na, Al, and Si, appear in the glass in the LLNL-S29 material. The differences in the nepheline composition and glass distribution can be ascribed to the levels of reduction in the two forms and the effects of consolidation by uniaxial hot pressing (HUP) at 1100 to 1200°C for the LLNL-S29 form versus HIP consolidation at 1040°C for the RSC-S29 material. The more reduced LLNL-S29 requires trivalent Al to form spinel with the Ni, Mn, and Fe in the waste. This tends to draw Al away from the alkali-silicate liquid phase formed during consolidation, making this phase silica rich. This, combined with the higher-temperature HUP process, causes a stoichiometrically pure nepheline to crystallize from the liquid phase which is surrounded by amorphous material upon cooling. The RSC-S29 ceramics formed by HIP at a lower temperature, with less reduction, are Al rich (evidenced by

trace corundum formation) and do not show a significant separate glass phase.

The three ceramic forms described above have distinctly different phase compositions and, to a degree, perform differently in short-term laboratory leach testing. However, long-term testing on the above forms has confirmed that they share a common mechanism of phase-specific dissolution, and that their behavior in aqueous environments can be described with some confidence based upon their determined phase compositions and microstructures and the data in the literature on the chemistry of natural minerals and pure phases.

C.2 PHASE-SPECIFIC INCONGRUENT DISSOLUTION

The main feature of the leaching behavior of the polyphase ceramics is that the forms show

phase-specific dissolution. That is, the individual crystalline grains in the forms react with aqueous environments in a manner very similar to their pure phase counterparts. The bulk properties of the ceramics become involved to the extent that the form itself will have a positive or negative surface potential (influencing reaction product formation), and that the grain size and spatial distribution affect leaching through geometric considerations. Each of these

points will be treated as the mechanistic description is developed.

The phase-specific nature of the dissolution process can be observed by several means. One approach is to compare the surface x-ray patterns of slides of the ceramics before and after leaching. Figure C.2 (A & B) shows two sets of before and after diffraction patterns taken in a long-term, 90°C, MCC-1 type leach test of the CSRL-60 and RSC-S29

SC84-26531

FIGURE C.2A. X-Ray Diffraction Patterns Taken from the Surface of a Slide of the CSRL-60 Ceramic Form Before and After Static Leaching in Deionized Water at 90°C for 816 Days. The dark shaded nepheline peaks are completely removed by leaching, the hatched product peaks correspond to a calcium aluminosilicate reaction product.

SC84-26530

RSC-S29 As
PREPARED SURFACE AFTER 632 DAYS IN
DEIONIZED WATER, 90°C

LEGEND

MP - MAGNETOPLUMBITE	P - PEROVSKITE	S - SPINEL
PB - PSUEDOBROOKITE	N - NEPHELINE	H - HAUYNE
Z - ZIRCONOLITE	M - MURATAITE	F - HEMATITE
	G - GIBBSITE	

FIGURE C.2B. X-Ray Diffraction Patterns Taken from the Surface of a Slide of the RSC-S29 SYNROC-D Type Ceramic Before and After Static 90°C Leaching in Deionized Water for 632 Days. The shaded nepheline peaks show limited dissolution; gibbsite appears as a reaction product.

ceramics. The major features of the patterns are the complete removal of the nepheline from the CSRL-60 ceramic surface after 816 days of leaching, compared with the limited decrease in the nepheline peak intensity and disappearance of the trace hauyne phase observed in the RSC-S29 sample after 632 days. No change in the relative intensities of the peaks for the other phases occurred for either ceramic. In addition, minor new peaks can be seen, corresponding to the appearance

of crystalline precipitation reaction products, $\text{Al}(\text{OH})_3$ on the RSC-S29 sample and an as yet unidentified calcium aluminosilicate on the CSRL-60 sample. These patterns give an overview of the dissolution process, that is, phase-specific leaching and precipitation reactions, with only nepheline-glass (and the trace soluble hauyne phase) showing any reaction in the time scale of the test. The elements released by nepheline and the associated intergranular glass, Na, Cs, Ca, Al, and

Si, are the primary participants in precipitation reactions. The XRD patterns also point out the effect of a limiting mechanism at work in the titanate ceramic to significantly slow the nepheline dissolution compared to that observed with the alumina-based form.

The leaching process can be seen much more dramatically through the use of transmission electron microscopy. By exposing ion beam thinned foils (50 to 100 nm thick) of the ceramics to water for short time scales, the dissolution processes can be observed at the single-grain level (Harker et al. 1981; Clarke 1981). Figures C.3 and C.4 show comparison transmission electron micrographs of the two titanate ceramic forms before and after leaching as thin foils (Harker et al. 1982b; Morgan et al. 1984). The bright field micrographs show the fine grain nature of the ceramics, while the dark field micrographs highlight the amorphous material and areas where dissolution has occurred. The common feature between the ceramics is that only the

FIGURE C.3A. Transmission Electron Micrograph of a Thin Foil of the Lawrence Livermore National Laboratory, LLNL-S29, SYNROC-D Type Ceramic Form. The bright field micrograph, taken before leaching, shows the fine grain nature of the ceramic. The phases are labeled: nepheline (N), zirconolite (Z), magnetoplumbite (MP), and spinel types (S). Not all phases are shown. Note electron beam damage occurring to nepheline phase.

FIGURE C.3B. Transmission Electron Micrograph of the Rockwell International Science Center RSC-S29 Ceramic Form. The bright-field micrograph shows the increased magnetoplumbite (MP) and the presence of corundum (C), and murataite (M). Perovskite (P), zirconolite (Z), and nepheline (N) are present.

nepheline grains and surrounding areas show dissolution effects. The most noticeable difference is the degree of leaching. The LLNL-S29 shows some nepheline dissolution and complete removal of material surrounding the nepheline grains, while the RSC-S29 material shows only limited nepheline dissolution, with no intergranular phase leaching. The difference in behavior is the extent and distribution of amorphous material in the forms. The LLNL-S29 ceramic shows pockets of glass surrounding the nepheline grains, while the RSC-S29 material shows only minimal amorphous material. The CSRL-60 ceramic (Figure C.5) is extremely fine grained with continuous nepheline and intergranular amorphous material. The CSRL-60 material shows extensive intergranular dissolution from the continuous glass phase in thin foil leaching.

C.3 SATURATION AND PHASE DISTRIBUTION EFFECTS IN CERAMIC LEACHING

The XRD patterns in the previous section showed that after about 2 years of static

FIGURE C.4A. Dark-Field Transmission Electron Micrograph Taken of a Thin Foil of the LLNL-S29 Form After Leaching for 4 Hours at 90°C in Deionized Water. The ceramic shows distinct dissolution (light area) of amorphous material in the regions surrounding the chains of nepheline grains. The nepheline also shows some dissolution.

90°C leaching the RSC-S29 ceramic still had ample nepheline near its surface to give a good diffraction pattern, while the nepheline in the CSRL-60 ceramic was fully dissolved in the near-surface region. Since the Cu x-ray source used has a analysis depth on the order of a micron or less, it can be stated that the nepheline in the RSC-S29 was not uniformly leached to that depth. This is inconsistent with the known dissolution kinetics of nepheline (Tole and Lasaga 1981; Tole 1982) and the evidence of the solution alkali levels from the static leach tests of the CSRL-60 and RSC-S29 forms, which indicated that the ceramics should have experienced nepheline leaching to depths of about 15 and 5 microns respectively (assuming uniform phase distribution). The only satisfactory explanation for the disagreement between the XRD and solution data is that the nepheline in the RSC-S29 is not uniformly distributed and is physically encapsulated on a microscopic level by the more stable crystalline phases.

FIGURE C.4B. Dark-Field Transmission Electron Micrograph of a Thin Foil of the RSC-S29 Ceramic After Leaching 4 Hours at 90°C in Deionized Water. In contrast to the LLNL-S29, the RSC-S29 material shows no glass dissolution and only slight attack on the nepheline grains. Neither form showed any dissolution of non-silica-containing phases.

Figures C.6A and C.6B show plots of the normalized release versus $\log(\text{time})$ for the elements observable in solution in static leaching of the RSC-S29 form in deionized water. The plots indicate nepheline dissolution occurring at the exposed surface in the first days of testing, followed by precipitation reactions involving Al, Ca, Si, and eventually alkali. The time scale over which the effects of precipitation reactions and physical encapsulation appear is shown in Figure C.7. This Arrhenius plot of the average normalized leach rate of Na in the RSC-S29 ceramic shows excellent agreement with the pure mineral phase dissolution kinetics observed by Tole (Tole and Lasaga 1981; Tole 1982) at low temperatures and for the first three days at 90°C. The solid line in the figure indicates the first order dissolution behavior predicted by the low temperature and short term leach data, which give an activation energy of 16 kcal/mole at a pH of 7.2. The longer-term data, taken at 90°C, fall monotonically below the first order line, demonstrating the onset of a dissolution limiting process after only 3 days in solution.

These results are significantly different from the observations of experimentalists (Oversby 1982; Barkatt et al. 1983) who have carried out leach tests with crushed samples.

FIGURE C.5. Bright-Field Transmission Electron Micrograph of the Extremely Fine Grained CSRL-60 Ceramic Form. The open arrows show small uraninite grains encapsulated in corundum and the dark arrows show the continuous mottled, beam damaged, glass-nepheline phase.

FIGURE C.6. The Normalized Elemental Release of the Observable Elements Leached from the RSC-S29 Ceramic Formulation Versus Log Time to 632 Days of Static MCC-1 Type Testing at 90°C in Deionized Water. U was below detection (<0.005 ppm) over the full range of the test. Na, Al, and Si concentrations are dominated by precipitation reactions after 200 days.

FIGURE C.7. Arrhenius Plot of the Na Release from the RSC-S29 Ceramic Showing the Effect of Rate-Limiting Mechanisms at 90°C After Less Than 3 Days. The solid line shows the excellent agreement between the release rate of Na from the ceramic form and natural nepheline (Tole 1982). The calculated activation energy for nepheline dissolution at a pH of 7.2 is 16 kcal/mole.

In these tests, under flow conditions, the nepheline and glassy material show steady-state dissolution kinetics with alkali release sufficient to drive the pH up above 9 with the titanate ceramics and above 11 for the alumino-silicate ceramic forms. In static testing with crushed samples^(a) the same pH rise is observed, but the normalized elemental release for the leaching species drops significantly with increasing SA/V as precipitation of alkali-alumino-silicates is enhanced; Table C.5. This contrasts with the slow alkali release and limited pH rise observed in static testing with the RSC-S29 monolithic samples (even at SA/V ratios of 50 m⁻¹). These results again indicate that microscopic physical encapsulation of nepheline is occurring in the monolithic SYNROC-D type ceramics, and that fracturing them preferentially exposes the silicate phases, enhancing dissolution.

(a) A. B. Harker, J. F. Flintoff and D. R. Clarke. 1984. "Leaching Mechanisms in Polyphase Ceramic Nuclear Waste Forms." To be submitted to *J. Am. Ceram. Soc.*

The property of the titanate-silicate ceramics which leads to the encapsulation of the nepheline-glass phase is the relatively low temperature eutectic of nepheline in comparison to that of the titanates. Nepheline forms out of a liquid phase in the ceramics at temperatures above about 900 to 950°C and can flow into voids in the consolidating green body, forming pockets. This phenomenon was studied by Clarke and Flintoff (1983), who demonstrated that the green density used in processing ceramic waste forms can change the observed nepheline-glass leach rate in monoliths of exactly the same composition and final density by a factor of two in 96-day static testing. They also observed that the ceramics exhibited extremely localized nepheline leaching, producing craters whose dimensions increased with decreasing green density (Figure C.8). Further, the microscopic studies clearly showed that precipitates preferentially formed in the vicinity of the leached craters, indicating that localized saturation concentrations are reached in the microscopic regions where nepheline-glass dissolution occurs. Such saturation in the craters could also impede the progress of the leaching process into the veins of soluble material, further stabilizing encapsulated pockets of nepheline, even if they are connected by tortuous pathways to the exposed surface. Note in Figure C.8 that the regions between the craters left by nepheline dissolution exhibit no visible effects from the water exposure.

C.4 REACTION PRODUCTS IN CERAMIC LEACHING

The formation of solid reaction products from leaching of the ceramics is dependent upon both the temperature range and aqueous environment. In the SYNROC-D ceramics for T < 100°C, the nepheline, glass and an ulvo-type spinel in the LLNL S29 type are the only phases which show significant dissolution and product formation on laboratory time scales. However, in the alumina-silica based ceramics there is some surface reaction of the uraninite and corundum in addition to the dissolution of the nepheline-glass phase. Under hydrothermal conditions (300-400°C) more extensive reactions of the silicate phases occur and some reaction of perovskite has been observed with the titanate materials (Sheetz, White and Atkinson 1982).

To a great extent the observable products in the laboratory leaching of both the titania and alumina based polyphase ceramics are controlled by the dissolution of the nepheline and glass phases as well as the initial aqueous environment. Figure C.9 shows a plot of the stability fields of some minerals in the NA-Al-Si-O-H-Cl system (Tole 1982). To

TABLE C.5. Normalized Elemental Release (g/m^2) Data Taken in 28 Day Static Testing of Crushed RSC-S29 Ceramic Samples as a Function of SA/V Ratio. The tests were run at 90°C in initially deionized water (Harker, Flintoff and Clarke 1984)

Element	SA/V, m^{-1}							
	360	700	1,710	2,830	3,440	4,450	7,160	10,600
Na	3.16	0.98	0.76	0.54	0.58	0.46	0.36	0.35
Al	0.18	0.11	0.059	0.047	0.045	0.018	0.029	0.032
Si	0.68	0.33	0.13	0.093	0.092	0.045	0.048	0.044
Ca	0.15	0.033	0.013	0.006	0.006	0.015	0.002	0.001
Ti	<0.001	<0.0005	<0.0003	<0.0002	<0.0001	<0.0001	<0.0001	<0.00009
Mn	0.0029	<0.0012	<0.0007	<0.0003	<0.0004	<0.0002	<0.0002	<0.00009
Fe	0.00081	0.00066	0.00031	0.00021	0.0002	0.00012	0.00017	0.00011
Ni	0.0086	0.0059	0.0029	0.00087	0.0014	0.00043	0.00052	0.00018
Sr	<0.065	<0.027	<0.016	<0.0066	<0.0081	<0.0048	<0.0039	<0.002
Zr	<0.007	<0.003	<0.002	<0.0007	<0.0008	<0.0005	<0.0004	<0.0002
Cs	1.48	0.26	0.15	0.11	0.10	0.099	0.055	0.065
Ce	<0.08	<0.032	<0.02	<0.008	<0.01	<0.006	<0.005	<0.0025
U	0.0014	0.00032	0.00032	0.0057	0.00031	0.00021	0.00031	0.00050
pH	8.20	8.42	8.73	8.83	9.02	8.45	9.25	9.25

FIGURE C.8. Comparison SEM Micrographs of the Leach Surfaces of Three Samples of the RSC-S29 Ceramic After 96 Days of Static, 90°C, Deionized Water Leaching. The samples had initial green densities of about 25, 35, and 45% respectively from left to right. The lower green density sample shows longer and deeper leached craters than observed in the higher green density samples. Note localized precipitation and residual grains of stable phases (Clarke and Flintoff 1983).

FIGURE C.9. Stability Fields of Some Natural Minerals in the System Na-Al-Si-O-H-Cl. Taken from Tole (1982). The shaded areas show the regions of static and flow laboratory leach tests and natural ground waters.

obtain a two-dimensional representation, the figure was plotted assuming the initial presence of gibbsite, with Al not considered as a separate variable. Laboratory deionized water tests begin in the stability range of gibbsite, which has been observed by XRD as a surface precipitate in the titanate ceramics. However, as the dissolution continues and the alkali and pH rise the stability field moves toward aluminosilicates such as kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), paragonite ($\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) and albite ($\text{NaAlSi}_3\text{O}_8$). The shaded areas show the regions of the plot pertaining to the various types of laboratory tests.

Reaction product analyses on the titanate based ceramics, in leach tests with $T < 100^\circ\text{C}$, are primarily based upon XRD and SEM/EDXS analyses. In deionized water leaching experiments, both static and flowing, Al-rich precipitates with XRD peaks corresponding to gibbsite have been observed (Harker, Flintoff and Clarke 1984; Ryerson, Bazan and Campbell

1982). However, in the longer-term and silicate water leaching tests, precipitates containing Si, Ca, K, and Cs as well as Al have been found. The micrographs in Figure C.10 show the nature of the leached RSC-S29 ceramic surface. Large areas of zirconolite, murataite, magnetoplumbite, and spinel show no reaction, with craters marking where the nepheline pockets have been removed. In the magnified view of the craters small nodules of lighter contrast material can be seen. These nodules are clumps of zirconolite and other insoluble phases which were encapsulated by the dissolving nepheline as well as reaction products. SEM/EDXS can be used to separate out the individual phases. Gibbsite appears as highly Al-rich crystallites along with individual clumps showing Ca as the only cation (Figure C.11), which have been identified as $\text{Ca}(\text{OH})_2$. Other localized precipitates were observed that showed high Ca and S concentrations. These were identified as CaSO_4 , forming from the dissolution of the soluble hauyne phase.

In long-term tests in simulated silicate ground water (Harker, Flintoff and Clarke 1984) a reaction product has been observed which contains Na, Cs, K, Al, and Si (Figure C.12). EDXS and XPS analyses of the material indicates a stoichiometry similar to a paragonite or muscovite-type phase, $(\text{Na,K,Cs})\text{Al}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$, as would be expected based on the stability field diagram in Figure C.9. The good agreement of the observed products with those found in pure phase studies of nepheline leaching again support the use of natural analogues to describe ceramic waste form dissolution.

The SYNROC-D type LLNL-S29 material contains the only titanium phase with demonstrated solubility below 100°C , an ulvo-spinel which is less stable than the magnetite-type spinel of the RSC-S29 ceramic. This phase shows some loss of intensity in its XRD peaks after leaching in deionized water, with the resulting release of Ti and Fe leading to the formation of hoegbomite, nominally $\text{Fe}^{2+}_{0.78}\text{Mg}_{0.71}\text{Fe}^{3+}_{0.34}\text{Ti}_{0.26}\text{Al}_{3.46}\text{Si}_{0.04}(\text{OH})_8$. This phase can be seen forming in the leached area of an early SYNROC-D sample in the dark-field TEM micrograph in Figure C.13, taken from a thin foil leached for 24 hours in deionized water (Clarke 1981). Hoegbomite is a natural mineral, which forms in association with corundum, spinel, and titaniferous magnetite (Friedman 1952) as a replacement product for ulvo-type spinels.

Leach testing in synthetic brine ground water containing Mg and Cl showed both the alumina-silica-based ceramics and the titanate forms

FIGURE C.10. SEM Micrographs of the Surface of a Sample of the RSC-S29 Ceramic After 200 Days of 90°C Static Deionized Water Leaching. The regions between the nepheline pockets show no dissolution. The higher magnification views of the leached zones show the porous surface layer formed in the craters from residual grains of stable phases and reaction products.

to be preferential locations for the precipitation of a mixed magnesium oxychloride, $\text{Mg}_2(\text{OH})_3(\text{Cl})4\text{H}_2\text{O}-\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_25\text{H}_2\text{O}$. This phase was identified by both XRD and XPS analysis and was found to form a honeycomb-like deposit over the full surface of the ceramic forms (Figure C.14). The precipitation reaction was apparently induced by the surface charges on the ceramics, in that gold foil strips in the solution showed no surface layer (Jantzen et al. 1982).

The dissolution processes occurring in the alumina-silica ceramics have been discussed in detail in the literature (Jantzen et al. 1982) and have been shown to be very phase-specific. Nepheline and corundum are the only two phases which show clear reaction product formation. Corundum in pure water has been demonstrated to form a fibrous scale of boehmite, $\gamma\text{-AlO}(\text{OH})$. Boehmite is thermodynamically favored over gibbsite at temperatures above 100°C, but appears as the

FIGURE C.11. SEM/EDX Characteristics of $\text{Ca}(\text{OH})_2$ Nodules Formed in the Leaching of Nepheline from the RSC-S29 SYNROC-D Type Ceramic

preferred product on the high-alumina-content ceramics even at lower temperatures (Jantzen et al. 1982; Robie, Hemingway and Fisher 1979). This process of boehmite scale formation was observed by STEM in thin foil leach test as is shown in Figure C.15, and has been confirmed by XRD identification of the product. The formation of the boehmite scale on the exposed corundum lowers the free energy of reaction, apparently stabilizing this phase.

The soluble nepheline phase (and associated amorphous material) release alkali, Al, Ca and Si into solution, increasing the pH and moving the system toward the stability range of alkali-alkaline earth-alumino-silicate precipitates as found in the titanate system. The XRD pattern in Figure C.2A shows two major product peaks on the CSRL-60 material in long-term static testing. Combining this with the EDXS analysis shows the

FIGURE C.12. SEM/EDX Characteristics of the Major Alkali-Alumino-Silicate Reaction Product Formed in Long-Term Static Testing of the RSC-S29 SYNROC-D Type Ceramic. The crystallite has a stoichiometry similar to paragonite $(\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2)$.

major product to be a calcium alumino-silicate, as yet unidentified. However after 28 days of leaching at 150°C , XRD analysis shows an identifiable calcium-alumino-silicate of the stratlingite type, $\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot 8\text{H}_2\text{O}$ (Harker and Clarke 1982; ICDD 1983).

The other phases in the CSRL-60 ceramic are quite stable at temperatures under 100°C . The hercynite spinel showed no alteration in laboratory tests, and the magnetoplumbite showed only minor ion exchange reactions giving up alkali for hydronium. The uraninite phase shows surface oxidation in deionized and silicate waters with high oxygen content and some U^{6+} is released into solution during short term testing. Solution analyses, however, show very little soluble U in the long term tests, <0.005 ppm after 2 years, and XRD

FIGURE C.13. Transmission Electron Micrograph of a Leached Thin Foil of an Early SYNROC-D Type Ceramic Showing Hoegbomite Formation in Holes, Left by the Dissolution of Glass, and the Ulvo-Type Spinel (Clarke 1981)

FIGURE C.14. XPS Spectrum of a Mixed Magnesium Oxychloride Formed on the Surface of the CSRL-60 Ceramic Form During Static Simulated Brine Leaching at 90°C (Jantzen et al. 1982)

FIGURE C.15. Transmission Electron Micrograph of a Leached Thin Foil of an Alumina-Based Ceramic, Showing the Formation of a Boehmite Scale on Corundum Grains During 90°C Static Leaching (Jantzen et al. 1982)

analysis shows only slight broadening of the uraninite Bragg reflections, indicating some oxidation to $UO_{2.25}$ at the exposed surface. XPS analysis also shows uranium to be present in the top 5 nm of the CSRL-60 ceramic surface after 816 days of static leaching, indicating that the stable form of U at pH levels >9 is a solid or complexed precipitate. Under repository conditions, with pH levels above neutral and low Eh, uraninite would be expected to be chemically stable if high levels of carbonate were not present (Langmuir 1978).

The phase-specific forward and back reactions defined in the low-temperature studies are listed in Table C.6. The list is by no means inclusive, as the precipitation products are directly dependent upon the conditions of the aqueous environment.

C.5 HYDROTHERMAL REACTIONS OF CERAMIC WASTE FORMS

Hydrothermal leaching of the ceramic nuclear waste materials serves two distinct purposes. The first is to investigate the "worst case" scenario of the waste form being exposed to water in a sealed repository while still thermally hot. The second to determine what the "end member" saturation products might be

in different aqueous environments, in that the hydrothermal conditions accelerate dissolution and recrystallization. The relationship between hydrothermal tests and 25-90°C leach tests cannot be generalized. In some cases, the same reactions occur, only faster and with a closer approach to equilibrium. In other cases, the hydrothermal dissolution may be by a quite different mechanism. Hydrothermal testing provides, in any case, much additional insight into the dissolution process because reactions frequently go far enough that product phases can be identified in addition to the uptake of elements into solution. The data can also be directly linked to well established pure phase and geologic cases where hydrothermal studies have been extensive.

The equilibrium or saturation concentration of solids in aqueous solvents usually increases rapidly with increasing temperatures. There are some exceptions, e.g., substances with retrograde solubility. However, increased solubility is usually found in oxides, silicates, and related minerals. Some of the titanate phases have retrograde solubility, which is responsible for the excellent leach resistance of some of the SYNROC components under high temperature hydrothermal conditions. The increase in saturation concentration also increases the driving force for dissolution. A typical rate equation has the form

$$dc/dt = Ak(C_s - C)^n/V \quad (C.1)$$

where A = surface area, V = solution volume, k = forward reaction constant, C_s = saturation concentration, and n = reaction order. Increasing C_s increases the reaction rate.

The rate constants increase with increasing temperature according to the Arrhenius equation, in which activation energies for dissolution are typically in the range of 10 to 20 kcal/mole and reaction rates may increase by several orders of magnitude between a 70°C leach test and one run under hydrothermal conditions at 300°C.

Phase equilibria relations in the complex multi-component systems of nuclear wastes may be described by phase reaction lines on P-T space. Commonest of these reactions lines are those that describe hydration-dehydration reactions. The low-temperature phases in most silica-alumina-metal oxide systems are hydrated. Exceptions are titanates and zirconates which usually are not hydrated. As will be described, the bulk of the hydrothermal reactions observed in the RSC-S29 type SYNROC-D ceramics involved the

TABLE C.6. Products Formed in Phase Specific Dissolution of Polyphase Ceramic Forms at 90°C

Reacting Phase	Water	Product Phase	Nominal Stoichiometry of Product
Nepheline	Deionized	Gibbsite	$\text{Al}(\text{OH})_3$
Nepheline	Deionized	Calcium hydroxide	$\text{Ca}(\text{OH})_2$
Nepheline	Silicate	Paragonite-type	$(\text{Na}, \text{Cs}, \text{K})\text{Al}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
Hauyne	Deionized	Calcium sulfate	$\text{Ca}(\text{SO})_4$
Ulvo-Spinel	Deionized	Hoegbomite	$\text{Fe}_{0.78}\text{Mg}_{0.71}\text{Ti}_{0.26}\text{Al}_{3.46}\text{Si}_{0.04}(\text{OH})_3$
Solution	Mg brine	Mg oxychloride	$\text{Mg}_2(\text{OH})_3(\text{Cl}) \cdot 4\text{H}_2\text{O} - \text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$
Corundum	Deionized	Boehmite	$\text{AlO}(\text{OH})$

nepheline-glass phase and the observed products conform to expected silica-alumina aqueous reaction behavior, with the titanate and zirconate phases showing little reaction.

Samples of the Rockwell RSC-S29 ceramic forms were sealed in gold capsules with various water compositions (deionized, connate, NBT-6a Brine) and heated to 200, 300, and 400°C for 7 days (White 1982; Freeborn and White 1984). The reaction products and solution concentrations were determined. The general results indicated that the hydrothermal conditions accelerated the dissolution of the nepheline and trace hauyne phase and caused some corrosion of the perovskite phase. None of the studies indicated any dissolution on the primary actinide hosts phases zirconolite, magnetoplumbite, and murataite. Of the radionuclide simulants, Cs, Sr, La, Ce, U, and Th, in the ceramic form only U and Cs were found in measurable quantities in solution. The observed solution concentrations in the 7 day tests are listed in Tables C.7, C.8, and C.9. Note that the blank values for the elements have not been subtracted.

Reaction products were observable in the various tests by XRD and SEM/EDXS. The results are summarized in Table C.10. In the deionized water tests at 200°C small crystals of a wairakite-type phase were observed and some clay-like material. At 300°C the crystallization reactions were enhanced and well-formed crystals of analcime, containing Cs, were observed. In addition there was a phase with micaceous habit composed of Ca, Al, and Si. The EDXS analysis indicates the phases to be of the anorthite or margarite type. At 400°C the only identified product was a plagioclase feldspar, formed from the decomposition of the analcime phase. There were also very small crystallites present, possible a sphene phase, CaTiSiO_5 . The solution

data and SEM observations indicate that only the nepheline phase showed any significant reaction in the waste form and this was at a maximum in the 300°C experiments. At 400°C growth of the product phase is faster than the dissolution process depleting the solution of ions. The small amount of U in solution would be expected to come from limited reaction of the secondary actinide phase perovskite.

The reaction products in connate water (Langmuir 1978) at 200°C were identified as analcime and calcite plus a minor micaceous or clay phase. At 300°C reaction products were more abundant, with the analcime crystals growing larger and more calcite being present. The minor micaceous phase was no longer present. A third phase, present at 300°C, was not identified, but contained Ca, Ti, Fe, and presumable Na, and Al. At 400°C the analcime was replaced by a sodalite phase, and an Fe-rich phase, magnetite or maghemite, was also present.

In the high-Mg-content bittern brine tests (White 1982) the ceramic was found to be the most reactive. At 200°C a smectite was formed which at 300°C was replaced by a phase higher in Mg and Si, probably chlorite. At 400°C the chlorite type was still present and the Fe-rich magnetite or maghemite phase again appeared. A minor phase containing Ca and a rare earth (La or Ce) also was present, again indicating some reaction of the perovskite.

In general, the RSC-S29 type ceramic waste form was highly stable under hydrothermal conditions. The observed reactions were primarily from the nepheline phase with some contribution from the trace hauyne and from the perovskite. The Al in solution quickly saturates and aluminosilicates are precipitated as different minerals. In deionized

TABLE C.7. Solution Analyses for RSC-S29 Ceramic Hydrothermal Testing in Deionized Water. Reported in ppm by weight, except U reported as ppb by weight.

	Run No.					
	S29-Z (Blank)	S29-C 200°C	S29-A 300°C	S29-B 300°C	S29-D 400°C	S29-E 400°C
Al	2	12	18	100	6	44
Ca	4	11	14	18	21	10
Ce	<2	<2	<2	<2	<2	<2
Cs	<3	<3	31	<3	<3	<3
Fe	<2	<2	<2	4	<2	4
K	<2	4	6	6	4	21
La	<2	<2	<2	<2	<2	<2
Mg	<2	4	6	7	8	4
Mn	<2	<2	<2	<2	<2	<2
Na	5	85	250	250	125	125
Ni	<2	<2	<2	<2	<2	<2
P	<2	7	<5	6	<5	<5
Si	<5	34	47	70	52	75
Sr	<3	<2	<2	<2	<2	<2
Th	<5	<5	<5	<5	<5	<5
Ti	<2	<2	<2	<2	<2	<2
U (ppb)	30	30	90	30	<25	30

TABLE C.8. Solution Analyses for RSC-S29 Hydrothermal Leach Testing in Connate Water. Analyses are in ppm by weight except for U which is reported as ppb by weight.

	Run No.					
	S29-X (Blank)	S29-L 200°C	S29-O 300°C	S29-P 300°C	S29-R 400°C	S29-S 400°C
Al	4	21	185	165	4	4
Ca	3	24	11	19	12	17
Ce	<2	<2	<2	<2	<2	<2
Cs	<3	<3	13	22	49	43
Fe	<2	<2	8	<2	<2	3
K	4	49	19	85	36	27
La	<2	<2	<2	<2	<2	<2
Mg	<2	9	4	5	5	6
Mn	<2	<2	<2	<2	<2	<2
Na	2,500	2,600	3,000	3,000	3,100	3,100
Ni	<2	<2	<2	<2	<2	<2
P	<5	<5	<5	<5	<5	<5
Si	16	14	14	15	4	4
Sr	<2	<2	<2	<2	<2	<2
Th	<5	<5	<5	<5	<5	<5
Ti	<2	<2	<2	<2	<2	<2
U (ppb)	<25	350	100	110	70	30
Zr	<4	<4	<4	<4	<4	<4

TABLE C.9. Solution Analyses for Hydrothermal Leaching of the RSC-S29 Ceramic in NBT-6a Brine (White 1982). Analyses are reported as ppm by weight except for U which is reported as ppb by weight.

	Run No.					
	S29-Y (Blank)	S29-K 200°C	S29-H 300°C	S29-I 300°C	S29-J ^(a) 400°C	S29-Q ^(a) 400°C
Al	<2	<2	<2	<2	11	2
Ca	34,500	33,900	35,900	35,700	35,700	34,900
Ce	<4	<4	<4	<4	<4	<4
Cs	<3	12	45	41	57	50
Fe	>2	31	2	3	540	540
K	27,400	26,800	27,800	27,400	27,800	26,800
La	<2	<2	4	4	6	1
Mg	13,500	12,900	12,900	12,700	11,500	10,900
Mn	<2	2	27	24	240	260
Na	21,000	20,600	22,200	22,000	25,200	23,200
Ni	<2	<2	2	2	9	7
P	<5	10	<5	<5	300	290
Si	<5	75	180	185	<5	<5
Sr	<2	<5	9	9	29	33
Th	<5	<5	<5	<5	<5	<5
U (ppb)	100	110	10,600	16,800	470	440
Zr	<4	<4	6	9	<4	6

(a) A precipitate formed in these runs between the time of opening the capsules and analysis. It was removed by centrifugation, and was tentatively identified as iron hydroxide.

TABLE C.10. Products Formed in Phase-Specific Hydrothermal Reactions of Polyphase Ceramic Waste Forms

Reacting Phase	T (°C)	Water	Product	Nominal Stoichiometry
Nepheline	200	DI	Wairakite	$\text{CaAl}_2(\text{SiO}_3)_4 \cdot 2\text{H}_2\text{O}$
Nepheline	200	DI	Clay	
Nepheline	300	DI	Analcime	$\text{NaAlSi}_2\text{O}_6$
Nepheline	300	DI	Anorthite or margarite	$\text{CaAl}_2\text{Si}_2\text{O}_8$ $\text{CaAl}_4\text{Si}_2\text{O}_{11}(\text{OH})_2$
Nepheline	400	DI	Feldspar	
Nepheline & perovskite	400	DI	Sphene	CaTiSiO_5
Nepheline	200	Connate ^(a)	Analcime & clay	
Nepheline	200	Connate	Calcite	CaCO_3
Nepheline	300	Connate	Analcime & calcite	
Nepheline & perovskite	300	Connate	Unknown	Ca, Ti, Fe, Na, Al
Nepheline	400	Connate	Sodalite	$\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$
Nepheline & perovskite	300	Connate	Maghemite or magnetite	Fe_2O_3 or Fe_3O_4
Nepheline	200	Brine ^(b)	Smectite clay	$\text{Al-Si-O-OH-H}_2\text{O}$
Nepheline & perovskite	300	Brine	Chlorite	$\text{Na}(\text{AlMg})_7\text{Si}_8\text{O}_{20}(\text{OH})_{10}\text{H}_2\text{O}$
Nepheline & perovskite	400	Brine	Chlorite & maghemite or magnetite	
Perovskite	400	Brine	Uraninite	UO_2

(a) Connate water, alkali-silicate ground water (White 1982).

(b) Bittern brine, Mg-rich brine (White 1982).

water, these products are mainly analcime at lower temperatures and feldspars at higher temperatures. When other ions are present, such as Mg in bittern brine, different products such as chlorite are formed. Nepheline is not stable in the presence of water at lower temperatures and it reacts to consume silica from solution.

Calcium appears in several of the product phases, including smectite clays, and in sphene at 400°C. There is some Ca in the nepheline, which suggests some attack of the perovskite. The transition metals appear in solution only at 300 and 400°C and only in the high Mg brine. Hot bittern brines are extremely corrosive because of the precipitation of $Mg(OH)_2$ at high temperatures, leaving HCl in solution, lowering the pH. Only this hot acid appears capable of releasing the transition metals from their host phases spinel, murataite, and magnetoplumbite. The uranium extracted from the ceramic, presumably from perovskite, appears in solution, but is primarily reprecipitated as uraninite.

C.6 PURE PHASE AND NATURAL ANALOGUE BEHAVIOR

There is substantial evidence that nuclear waste ceramics dissolve at rates which are the weighted sums of the dissolution rates for the individual crystalline components. That is, synergistic effects are small at the low concentrations and slow rates typical of nuclear waste leach solutions.

This may be expressed as

$$R_i = V \sum_j \frac{1}{A_j} \frac{dC_i^j}{dt} \quad (C.2)$$

where R_i is the net rate of dissolution of radionuclide, i , V is solution volume, A_j is the effective surface area of phase, j , and dC_i^j/dt is the single phase rate of dissolution of radionuclide i from phase j . Recalling the discussion in previous sections about dissolution along grain boundaries and about encapsulating effects, the effective area, A_j , must be established with some care.

The dissolution kinetics of the following single phase radionuclide hosts have been investigated:

Nepheline	Tole (1982)
Spinel	Nacklas (1983)
Magnetoplumbite	Troester et al. (1984)
Zirconolite	Khalil (1984)
Perovskite	Khalil (1984)

The dissolution of all of these crystalline phases has been observed to follow a zero-order kinetics. That is, the concentration of a given radionuclide in solution increases linearly with time. Linear dissolution clearly cannot go on forever. Either the entire specimen dissolves, or some back reaction sets in. If the crystalline phase in question is stable in equilibrium with an aqueous solution, the back reaction is simply the precipitation of the same phase. The kinetics then move out of the linear regime and curve over asymptotic to the time-independent saturation concentration. A typical rate equation is equation (C.1).

In reality, not all of the proposed ceramic host phases are stable in equilibrium with an aqueous solution. These materials dissolve until concentrations in solution build up to the saturation level of some more stable phase after which there is the onset of a precipitation reaction. The reaction is one in which the original host phase reacts with water to form a precipitate phase. The rate is then described by an equation such as:

$$\frac{dC}{dt} = \frac{A}{V} k_+ - \frac{A'}{V} k_- (C - C_s) \quad (C.3)$$

where A = surface area of original phase, k_+ is the forward rate constant, A' is the effective surface area of the precipitate phase, k_- is the precipitation rate and C_s refers to the saturation concentration of the precipitate phase.

In all materials investigated, the dissolution mechanism in the acid regime was the attack of a proton onto the surface of the crystal. The forward rate constant was then a function of both pH and temperature. The temperature dependence was described by the usual Arrhenius equation and the pH dependence could be incorporated into the rate equation by separating the forward rate constant into two terms:

$$\frac{dC}{dt} = \frac{A}{V} k_+^* (a_{H^+})^n \quad (C.4)$$

The rate is then shown to be directly related to the hydrogen ion activity. In the acid regime, the empirical exponent $n = 1$, consistent with the proton attack mechanism. In the alkaline regime, n took on various negative values, usually in the range of -0.2 to -0.5 . No mechanistic explanation for this dependence has yet been surmised.

The sections that follow summarize the results obtained with the individual phases. For more detail on the specific experimental results, see the theses or publications from which these summaries are drawn.

C.6.1 Nepheline

Nepheline, $\text{NaAlSi}_3\text{O}_8$, is not stable in the presence of aqueous solutions at the pH and silica activity of normal ground water. As shown by Figure C.9, nepheline will react with water to form kaolinite or some other compound, the Na and part of the Si being taken into solution.

The rate of dissolution of nepheline was measured by analyzing the concentrations of Na, Si, and Al in solution as a function of time at constant pH for a variety of pH values (Tole and Lasaga 1981; Tole 1982). The dissolution was found to be surface reaction controlled and to obey a rate equation of the form C.3. Figure C.16 summarizes the results. Between pH = 3 and pH = 5, the rate increases linearly with hydrogen ion activity, that is, log rate is inversely proportional to pH. Between pH = 7 and pH = 11, the rate depends on the -0.2 power of the hydrogen ion activity. The exact functional form was not determined in the neutral pH "crossover" region. The temperature dependence of the dissolution rate follows the Arrhenius equation (Figure C.17). The activation energies are typical for surface reaction controlled kinetics.

Returning to Figure C.9, the initial stages in the dissolution process, when there is very little silica in solution, will have gibbsite as the stable precipitate phase when the system reaches aluminum saturation. As nepheline continues to dissolve, and the silica concentration increases, the system will reach saturation with respect to kaolinite which then becomes the precipitate phase. Figure C.18 shows the uptake of silica in solution and the change in apparent reaction rate when kaolinite becomes the precipitating phase. The change in the initial slope is not due to a change in the rate at which nepheline is dissolved, but represents slower increase of silica in solution because some of it is being removed by the precipitation of kaolinite. The first segment of the curve is described by only the forward reaction rate part of equation (C.3) and the slope gives the numerical values for the rate constant k_+ (after proper weighting for pH). The second segment of the curve reflects the effect of the second term in

equation (C.3) and its slope can be used to estimate the precipitation rate constant k_- .

C.6.2 Spinel

Nickel ferrite was chosen as a representative end member of the class of transition metal spinels that appear in many of the nuclear waste ceramics. Crushed ceramic pellets of NiFe_2O_4 were reacted with solutions of various pH and the reaction monitored by analyzing the solutions for Ni and Fe (Nacklas 1983). Spinel is a very stable phase and measurable concentrations were found only in solutions of pH = 3 or less.

The dissolution of spinel was found to follow linear kinetics as described by equation (C.4). Only the forward reaction rate was observed. There was no evidence for precipitates or of saturation effects on the time scale of the experiments. Nickel ferrite dissolves slowly in strong acids and the relative slopes of the dissolution curves for Ni and Fe (Figure C.19) suggest that the compound dissolves congruently. At pH = 3, the rate of uptake of Ni in solution is much higher than that of iron and at pH = 5.5 (all at 90°C) the dissolution of Ni is still measurable but the concentration of Fe is below detection limits (Figure C.20).

Figure C.21 summarizes the principal results. When these results are fitted to a rate equation (C.4), the value of "n" is 1.4 at pH less than 1.5 and n = 0.7 above pH = 1.5. The break occurs at approximately the pH where the solubility of iron falls rapidly due to precipitation of $\text{Fe}(\text{OH})_3$. The temperature dependence of the rates follow the Arrhenius equation with an activation energy of 22 kcal/mole.

The dissolution rate of nickel ferrite is a function of oxidation potential. The behavior described above is for experiments in air, with a value of Eh near the upper stability limit of water. When equivalent experiments are carried out in the presence of forming gas (5% H_2 + 95% N_2) bubbled over a palladium catalyst, the depression of iron dissolution disappears and the nickel/iron dissolution rates take on the 1:2 ratio expected from congruent dissolution. This is because of the stabilization of the more soluble Fe^{2+} species at low Eh. The effect of Eh on spinel dissolution is thus opposite to that found for technetium, uranium, and actinide species where low Eh decreases solubility. This is because the divalent states of the transition metals are generally more soluble than the trivalent states.

FIGURE C.16. Variation of the Measured Rates of Dissolution of Nepheline with pH and Temperature. The rates shown are initial Na release rates expressed as moles $\text{cm}^{-2} \text{hr}^{-1}$.

FIGURE C.17. Some Arrhenius Plots for Nepheline Dissolution

FIGURE C.18. Comparison Between Calculated (solid line) and Experimental (open circles) Values of Moles of Si in Solution at pH 7, 60°C. The arrow shows the point of transformation of gibbsite into kaolinite, calculated from thermodynamic data.

FIGURE C.19. Concentration Versus Time Plot for NiFe_2O_4 Dissolution at 90°C , $\text{pH} = 0$, $A/V = 0.185 \text{ cm}^{-1}$

FIGURE 20. Concentration Versus Time Plot for NiFe_2O_4 Dissolution at 90°C , $\text{pH} = 3$, $A/V = 0.5 \text{ cm}^{-1}$

C.6.3 Magnetoplumbite

The dissolution kinetics of one example of the magnetoplumbite structure was investigated (Troester, Freeborn and White 1984). The material was prepared as a sintered ceramic with about 85% of theoretical density. The chemical composition was

Crushed ceramic was dissolved in aqueous solutions of varying pH. Solutions were analyzed for Ca, La, and Al.

FIGURE 21. Plot of the Log of the Dissolution Rate of NiFe_2O_4 Versus pH . Rate is calculated from change in Ni^{2+} concentration with time.

The lanthanum hibonite representative of the magnetoplumbite structure dissolves in acid solutions according to a linear kinetics that likely represents a surface reaction controlling mechanism. The ratio of dissolution rates, $\text{Al}/\text{Ca} = 6$, suggests that calcium may be dissolved preferentially. The ratio of Al/La dissolution rates is approximately the same as the atomic ratio of the elements in the solid sample. Normalized leach rates are very low even in the acid solution.

Dissolution of $\text{CaAl}_{12}\text{O}_{19}$ in neutral and basic solutions is masked by the presence of a small amount of CaAl_4O_7 impurity phase which dissolves very rapidly and provides a nearly constant background concentration. The ions put into solution from dissolution of magnetoplumbite never rise above this background which then provides a maximum dissolution rate in the neutral and basic solutions.

C.6.4 Perovskite

According to Nesbitt et al. (1981), perovskite is unstable in the presence of aqueous silica due to the reaction:

Carbon dioxide in natural waters may also destabilize perovskite because of the reaction:

$$\text{CaTiO}_3 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} (\text{aq}) + \text{TiO}_2 + \text{H}_2\text{O}(\text{l})$$

perovskite rutile

The dissolution rates of perovskite in aqueous solutions depend on the temperature and pH of the solutions. They also showed strong

dependence on the damage level. Table C.11 compares the fractional release rate of crystalline (0 MWh), heavily damaged (2 MWh), and metamict (4 MWh) perovskite phases. The fractional release rates of calcium and uranium (which occupy the same lattice site) from metamict perovskite are similar. In neutral solutions the release rate of calcium from metamict perovskite is twice its release rate from the heavily damaged material, but the release rate from crystalline perovskite is below detection limits. In pH 1.32 solutions at 90°C, where crystalline perovskite dissolved also, the fractional rate of release of calcium and uranium is about 200-300 times higher from metamict perovskite than from crystalline perovskite.

C.6.5 Zirconolite

Zirconolite, $\text{CaZrTi}_2\text{O}_7$, appears to be one of the most stable phases in the SYNROC family of nuclear waste ceramics. Like other crystalline waste forms, it is subject to radiation damage and metamictization.

A ceramic zirconolite was synthesized as sintered pellets. The material was prepared with 0.1 mole fraction $^{235}\text{U}^{4+}$ substituted for

TABLE C.11. Comparison of the Fractional Release Rates from Perovskite Damaged to Different Levels^(a)

Initial pH	pH ^(b) f		Fractional Release Rate, cm ⁻² day ⁻¹		
			0 Mwh	2 Mwh	4 Mwh
1.32	1.32	Ca ²⁺	1.5 x 10 ⁻³	4.3 x 10 ⁻¹	4.3 x 10 ⁻¹
		U ⁴⁺	2.1 x 10 ⁻³	2.0 x 10 ⁻¹	3.4 x 10 ⁻¹
4.12	7.90	Ca ²⁺	--	4.3 x 10 ⁻⁴	8.2 x 10 ⁻⁴
		U ⁴⁺	--	--	1.1 x 10 ⁻⁵

(a) All data at 90°C.

(b) Final pH following drift during the experiment.

Zr⁴⁺ in the structure and the material irradiated in the reactor. Dissolution kinetics were determined by reaction with aqueous solutions at varying pH (Khalil 1984).

Concentrations of dissolved species were below detection limits in most of the experiments on zirconolite; only at pH 0.0 was there sufficient concentration to permit calculation of a rate constant. After 60 days in pH 1.32 at 90°C, the concentration of calcium and uranium in solution was 2 mg/L and 15 x 10⁻³ mg/L, respectively. Assuming that the concentration increased linearly with time, the calculated rates are 33 x 10⁻³ mg/L·day and 25 x 10⁻⁵ mg/L·day for calcium and uranium, respectively. The normalized fractional release rates were therefore 2.69 x 10⁻⁴ cm⁻² day⁻¹ and 3.45 x 10⁻⁵ cm⁻² day⁻¹ for calcium and uranium, respectively. At pH 4.12, both calcium and uranium were below limits of detection. The normalized fractional release rates for calcium and uranium from perovskite were 4.3 x 10⁻¹ cm⁻² day⁻¹ and 3.4 x 10⁻¹ cm⁻² day⁻¹, respectively (from Table C.11). This means that the normalized release rates for calcium and uranium from perovskite are 10³-10⁴ times their release rates from zirconolite. In other words, the zirconolite phase would be more suitable to host alpha-emitting radionuclides.

C.7 DISCUSSION AND CONCLUSIONS

The conclusion that can be drawn from the various tests of polyphase ceramics is that the controlling features of their dissolution mechanisms are threefold:

1. The individual phases perform as their pure phase counterparts, showing the appropriate dissolution kinetics and activation energies.

2. Precipitation reactions occur as expected over the full range of temperatures and water types tested, forming the natural mineral phases which are thermodynamically stable under the test conditions. There is no surface or "hydrous gel layer" formation as experienced with amorphous forms.

3. The distribution of the aluminosilicate phases in the ceramics controls the short-term leach behavior and the observed pH in deionized water testing. In ceramics which have a large volume fraction of continuously distributed aluminosilicates the leaching process continues until saturation is reached, monoliths performing similarly to powdered samples. In HIP consolidated titania-silica based ceramics, RSC-S29 type SYNROC-0, the distribution of the aluminosilicate phases in pockets causes the reaction process to slow well below the kinetic dissolution rate of the pure phases in monoliths. This is caused by microstructural encapsulation of the soluble phases by the insoluble titanates and spinel, and localized saturation occurring in the microscopic craters. In powdered samples ample surface area of the aluminosilicates is exposed for the process to proceed without any physical restriction on the leaching process.

These data indicate that the actinide phases have the excellent stability in aqueous environments predicted by their natural mineral analogues, which can also be used to establish the effects of transmutation and alpha recoil damage upon the forms. The dissolution and precipitation processes can be described in terms of pure phase reactions and all microstructural effects tend to slow the dissolution process rather than to accelerate them.

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