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Pacific Northwest
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A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford

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Prepared for the U.S. Department of Energy
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Summary

Privatized services are being procured to vitrify low-activity tank wastes for eventual disposal in a shallow subsurface facility at the Hanford Site. Over 500,000 metric tons of low-activity waste glass will be generated, which is among the largest volumes of waste within the U.S. Department of Energy (DOE) complex and is one of the largest inventories of long-lived radionuclides planned for disposal in a low-level waste facility. Before immobilized waste can be disposed, DOE must approve a "performance assessment," which is a document that describes the impacts of the disposal facility on public health and environmental resources. Because the release rate of radionuclides from the glass waste form is a key factor determining these impacts, a sound scientific basis for determining their long-term release rates must be developed if this disposal action is to be accepted by regulatory agencies, stakeholders, and the public. In part, the scientific basis is determined from a sound testing strategy.

The foundation of the proposed testing strategy is a well accepted mechanistic model that is being used to calculate the glass corrosion behavior over the geologic time scales required for performance assessment. This model requires that six parameters be determined, and the testing program is defined by an appropriate set of laboratory experiments to determine these parameters, and is combined with a set of field experiments to validate the model as a whole.

Three general classes of laboratory tests are proposed in this strategy: 1) characterization, 2) accelerated, and 3) service condition. Characterization tests isolate and provide specific information about processes or parameters in theoretical models. Accelerated tests investigate corrosion behavior that will be important over the regulated service life of a disposal system within a laboratory time frame of a few years or less. Service condition tests verify that the techniques used in accelerated tests do not change the alteration mechanisms. The recommended characterization tests are single-pass flow-through tests using a batch reactor design. Accelerated and service conditions tests include product consistency and pressurized unsaturated flow (PUF) tests. Nonradioactive glasses will be used for the majority of the laboratory testing (~80%), with the remainder performed with glasses containing a selected set of key radionuclides. Additionally, a series of PUF experiments with a natural analog of basaltic glass is recommended to confirm that the alteration products observed under accelerated conditions in the PUF tests are similar to those found associated with the natural analog. This will provide additional confidence in using the PUF test results to infer long-term corrosion behavior.

Field tests are proposed as a unique way to validate the glass corrosion and contaminant transport models being used in the performance assessment. To better control the test conditions, the field tests are to be performed in lysimeters (corrugated steel containers buried flush with the ground surface). Lysimeters provide a way to combine a glass, Hanford soil, and perhaps other engineered materials in a well-controlled test, but on a scale that is not practicable in the laboratory. The recommended field tests include some experiments where a steady flow rate of water is artificially applied. These tests use a glass designed to have a high corrosion rate so that it is easier to monitor contaminant release and transport. Existing lysimeters at the Hanford Site can be used for these experiments or new lysimeters that have been equipped with the latest in monitoring equipment and located near the proposed disposal site.

Glossary

ADT	accelerated dissolution test
ALT	accelerated leach test
ANL	Argonne National Laboratory
AREST-CT	Analyzer of RadionuclidE Source Term with Chemical Transport
ASTM	American Society for Testing and Materials
CPU	central processing unit
DLT	dynamic leach test
DOE	U.S. Department of Energy
EMSP	Environmental Management Science Program
GFLOPS	giga floating point operations per second
HLW	high-level waste
ILAW	immobilized low-activity waste
ISO	International Standards Organization
LAW	low-activity waste
MIIT	Materials Interface Interaction Test
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
PUF	pressurized unsaturated flow
RH	relative humidity
SPFT	single-pass flow-through test
STOMP	a nonisothermal, multiphase flow simulator
STORM	Subsurface Transport Over Reactive Multiphases
S/V	surface area-to-solution volume ratio
VHT	vapor hydration test
WIPP	Waste Isolation Pilot Plant

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1.0 Introduction

The Hanford Site in southeastern Washington State has been used extensively to produce nuclear materials for the U.S. strategic defense arsenal by the U.S. Department of Energy (DOE) and its predecessors, the U.S. Atomic Energy Commission and the U.S. Energy Research and Development Administration. A large inventory of radioactive and mixed waste has accumulated in 177 buried single- and double-shell tanks. The DOE is proceeding with plans to permanently dispose of this waste (Ecology 1996; 62 FR 8693). Liquid waste recovered from the tanks will be pretreated to separate the low-activity fraction from the high-level and transuranic wastes. The small volume of high-level immobilized waste and the much larger volume of low-activity waste (LAW) will be disposed of in different locations. The high-level waste (HLW) will be stored on the Hanford Site until sent to a federal geologic repository. The immobilized low-activity waste (ILAW) will be placed in a near-surface disposal system on the Hanford Site.

Privatized services are being procured[a] for treating and immobilizing the tank waste. The leading processing option for waste immobilization is vitrification. Vitrifying the LAW is expected to generate over 500,000 metric tons or 200,000 m^3 (6,000,000 ft^3) of LAW glass that will be disposed of under this plan. This is among the largest volumes of waste within the DOE complex and is one of the largest inventories of long-lived radionuclides planned for disposal in a low-level waste facility.

Before the immobilized waste can be disposed, DOE must approve a "performance assessment," which is a document that describes the long-term impacts of the disposal facility on public health and environmental resources. Results from an interim performance assessment have recently been published (Mann et al. 1998). A major conclusion from this study is that the release rate of radionuclides from the glass waste form by reaction with water is one of the key parameters that determines the impacts of the disposal action and is the most uncertain. Consequently, a sound scientific basis for determining the long-term release rates of radionuclides from these glasses must be developed if this disposal action is to be accepted by regulatory agencies, stakeholders, Native Americans, and the public.

A general approach for the evaluation of materials behavior in a disposal site has been developed that outlines logical steps to validate and confirm the corrosion behavior of materials whose life expectancies must greatly exceed the length of time over which experimental data can be obtained (ASTM 1991). These steps include determining the likely range of environmental factors in the disposal system, identifying and characterizing materials that are likely to be present in the disposal system, performing tests under site-relevant conditions to determine important alteration processes for those materials, developing models for key alteration processes, and performing tests that accelerate those processes. The ASTM protocol also recommends tests to confirm the corrosion model and to utilize information provided by analog materials or systems. Many steps in this approach relevant to waste glass behavior in general have been completed in studies conducted for deep geologic disposal systems and can be directly applied to the Hanford system. For example, the processes that control glass corrosion are well

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[a]Request for Proposals (RFP) No. DE-RP06-96RL-3308. Letter from J.D. Wagoner to Prospective Offerors, Department of Energy, Richland, Washington, February 20, 1996.

understood, and rate expressions have been developed and tested. What remains is primarily to characterize the specific corrosion behavior of actual LAW glasses. This includes identifying (or confirming) the corrosion processes that will control the long-term behavior of the glasses and release of radionuclides, measuring parameters needed to perform model calculations for performance assessment, and conducting accelerated and service condition tests to confirm and provide confidence in those calculations.

The purpose of this report is to document a technical strategy developed by Pacific Northwest National Laboratory (PNNL)[a] and Argonne National Laboratory that the ILAW disposal program will pursue over the next several years to evaluate the long-term radionuclide release behavior of the LAW glass(es) under development by the private contractors. As such, this document is intended to serve as the technical basis for the glass testing program that is needed to complete the performance assessment for the ILAW disposal facility. Specific matrices of tests will not be developed in this report; these are to be provided in separate test plans for each test method. However, this document will define the general classes of tests for which test plans will need to be developed and provide a general range of appropriate conditions for these tests. We begin the discussion of the technical strategy with a brief overview of the disposal system design and expected environmental conditions at the site.

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2.0 Disposal System Description

The Hanford Site is a 1450 km^2 area of semi-arid land located in southeastern Washington state. Average annual precipitation is 16 cm, with 44% of this total occurring during November, December, and January. Daytime high temperatures in summer can exceed 40°C, while outbreaks of arctic air masses in winter can cause temperatures to drop below -18°C. Plans call for the disposal system to include a protective surface barrier with design elements to minimize root intrusion, animal intrusion, and water infiltration. The use of silt-loam soils when combined with a representative community of shrub-steppe vegetation has been shown to cause most precipitation falling on the region to be lost through evapotranspiration. Consequently, the disposal facility is to be located in relatively dry, unsaturated soil, and performance assessment models must be applicable to the specific physics and chemistry of this type of system.

2.1 Water Infiltration

Water flow in the near-surface unsaturated zone is transient because of intermittent precipitation events. Transient water flow begins when water enters at the ground surface and infiltrates downward into the soil column. At some distance from the ground surface, transient effects will dampen out, and the downward flowing water will reach a steady infiltration rate. The distance at which steady infiltration occurs is sometimes referred to as the penetration depth (Eagleson 1978; Salvucci, 1993). Thus, the unsaturated zone essentially comprises two regions: an unsteady-flow region between the ground surface and penetration depth, and a steady-flow region between the penetration depth and the saturated zone water table. The steady flux in the lower unsaturated region is equal to the annual rate of ground-water recharge and therefore is composed of contributions not only from the most recent pulse, but from previous precipitation events as well.

The ILAW disposal facility will be situated below the penetration depth in the region of steady flow. The natural rate of moisture infiltration is approximately 3.0 mm/year (Fayer and Walters 1995). However, the natural rate of moisture infiltration cannot be relied upon because construction of the disposal system will destroy the natural soil-sediment profile and remove surface vegetation. Consequently, a protective surface barrier will be engineered with sediment layers and a capillary barrier to prevent or minimize infiltration. The design basis for the Hanford barrier (Myers and Duranceau 1994) specifies that less than 0.5 mm/year will pass through the barrier for the first 1,000 years. Infiltration beyond the root zone is controlled at the soil/atmosphere interface where surface soils and sediments, and vegetation, interact with the climate. The frequency, duration, and magnitude of precipitation and runoff events determine the infiltration rate. Infiltration into the disposal facility will be controlled by the physics described above, the unsaturated hydraulic properties of the surface and subsurface barriers to infiltration, the vault and surrounding soil, and the matric and gravity potential gradients.

2.2 Facility Description

A detailed design for the ILAW disposal facility is not yet available. However, Burbank (1997) has performed preconceptual engineering studies of alternative designs. The basic design unit for all the disposal facility concepts is a vault bay. The vault bays have concrete walls, floors, and ceilings. Six vault bays form a vault row. The number of vault bays depends on the size of the immobilized LAW containers and the spacing between containers. Burbank optimized the interior dimensions around the presumed dimensions of the waste package, 1.8 m × 1.2 m × 1.2 m ± 0.2 m (DOE-RL 1996), producing interior dimensions of 20 × 20 × 7.5 m. He also separates the vault rows and places a road between the two sets of vault rows (see Figure 2.1). This design accommodates a single vault capacity of 5040 waste packages in an array 10 wide × 6 high × 84 rows, with 19 vaults total at the disposal site.

All the concepts include backfilled soil around and on top of the waste containers in the facility. The soil was included in these concepts 1) for structural support, 2) to wick moisture away from the waste containers, and 3) to provide radiation shielding for the facility workers. They also have a similar barrier philosophy. The uppermost barrier is the surface barrier, which consists of sand/gravel layers to work as a capillary break, a layer (that may or may not be included in the final design) for conditioning the chemistry of the water to help minimize the rate of glass corrosion and/or radionuclide release, and a layer of basalt riprap to deter burrowing animals, plant root intrusion, and inadvertent intruders. Beneath the surface barrier, another sand-gravel capillary break will divert moisture coming through the surface barrier away from the vault. This barrier combination minimizes the amount of water that enters the vault.

The disposal vaults are to be located approximately 15 m below the top of the surface barrier. At this depth, the ambient temperature is approximately 15°C, and temperature fluctuations are

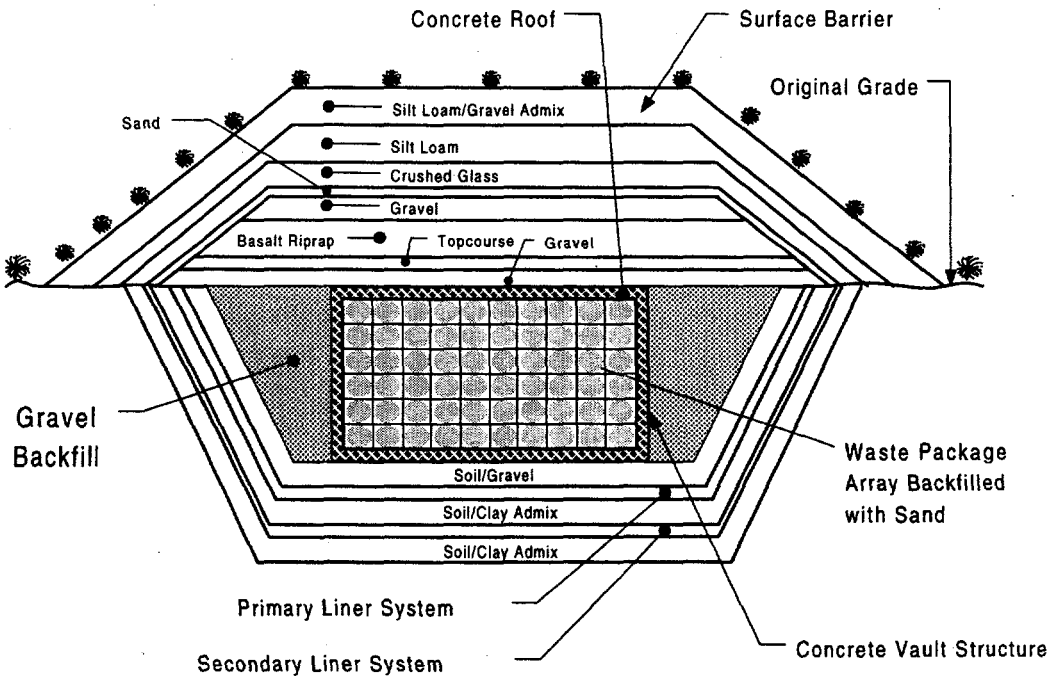

Figure 2.1. Schematic of LAW Disposal System

less than 2°C. Also, because the LAW generates a small amount of heat from radioactive decay (McGrail and Mahoney 1995), the disposal system can be treated adequately as an isothermal system. The waste packages are expected to consist of a rectangular steel container that holds the glass and possibly a filler material. The glass will likely not be annealed and thus will be thermally stress fractured to some extent. The extent of fracturing is important because it increases the available surface area for possible contact by water and thus can potentially increase the radionuclide release rate from the disposal system.

Based on this disposal system concept, small amounts of water are expected to percolate through the disposal system and eventually penetrate the steel containers and contact the glass. The goal of the glass testing program then, is to provide the necessary supporting data so that the radionuclide release behavior of this system can be modeled with sufficient confidence to support an overall performance assessment for disposal of ILAW at the Hanford Site.

3.0 Modeling Approach

Because it is impossible to formulate a rationale and a defensible testing program without understanding the physical and chemical processes that govern glass corrosion and radionuclide release as well as the conceptual models that describe these processes, we briefly review these concepts below.

3.1 Glass Corrosion Process

Fortunately, much is known about glass/water reaction processes. Glass forms ranging from simple binary and ternary silicate glasses to complex waste glasses with 30 or more components have been studied for 35 years. Much of this work relevant to silicate waste glasses has recently been compiled and critically reviewed (Bates et al. 1994). A general picture of the glass corrosion process in water has emerged that can be summarized as follows: upon initial contact by water, alkali is extracted by ion exchange in what is thought to be a diffusion-controlled process. Simultaneously, hydrolysis and dissolution of the glass network occurs. In unsaturated disposal systems where water content and flow rate are expected to be very low, the rate of ion exchange and dissolution decrease, but for different reasons. The ion-exchange rate slows in accordance with a diffusion-controlled process as a reaction layer builds up on the glass over time. A reaction layer builds up as a result of silanol condensation reactions that reform Si-O bonds. The dissolution rate of the glass network slows because of the common ion effect, i.e., as the solution becomes more concentrated in glass components, the difference in chemical potential between the glass and aqueous phase decreases, which decreases the dissolution rate. The dissolution rate cannot become zero because silicate glasses are thermodynamically unstable in water.

3.1.1 Importance of Secondary Phases

As a solution in contact with a dissolving glass becomes more and more concentrated in glass components, solubility limits for alteration phases begin to be exceeded. Although no generally accepted theory has been proposed to describe the factors controlling nucleation and growth, ultimately, the glass transforms into a paragenetic assemblage of alteration products or minerals. Also, no generally accepted theory exists that can be used to predict which specific phases should form or the sequence of their formation. However, from the Simplexity Principle (Goldsmith 1953), we know that the most disordered phase should form from a random system of components first. We know from the Ostwald Step Rule (Ostwald 1897) that subsequent transformations to more stable phases should occur in steps where the reaction products obtained at each step lay near the previous state in free energy. These governing principles have extremely important implications for the testing strategy because at the low temperatures (15°C) relevant for the LAW disposal system, metastable and/or amorphous phases may persist for long periods of time. Consequently, a means must be found for accelerating the transformation process during laboratory testing without altering the fundamental transformation process itself.

The secondary phases that form from the glass/water reaction process are expected to depend principally on the composition of the glass and not on other components in the disposal system

because the glass supplies the majority of the elements to the fluid from which the secondary phases precipitate. However, the water conditioning layer, filler material in and/or between waste packages, and the concrete used in vault construction may also impact the formation of secondary phases, especially in localized regions. Glasses that are stable with respect to the formation of alteration products will maintain a slow but finite rate of network hydrolysis and dissolution indefinitely. Many existing natural glasses exhibit these characteristics, having withstood weathering over geologic time scales. Laboratory tests have generally reproduced the same types of alteration products that have been found on these glasses (Grambow et al. 1986; Luo et al. 1997), confirming their long-term stability with respect to forming alteration phases. However, glasses that are unstable with respect to alteration product formation exhibit autocatalytic reactivity, i.e., a very rapid increase in dissolution rate that is limited only by the availability of water or the forward reaction rate of the glass, whichever is the rate limiting process. High-level waste glasses (Van Iseghem and Grambow 1988 have exhibited this phenomenon and so has a representative LAW glass, LD6-5412 (McGrail et al. 1997a). Consequently, the laboratory testing program must ensure that the LAW glass(es) being produced by the private vendors fall into the former, stable category. If not, then the tests should provide guidance for modifying the glass composition into a region with known long-term stability.

3.1.2 Effect of Ion Exchange

Because of the large effect that secondary phase formation has on glass dissolution rates, recent work on glass/water interactions has focused on understanding this process and incorporating it into models (Ebert and Bates 1993). The ion-exchange process has been largely ignored because it has been thought to be a short duration, secondary, or tertiary process that had little or no bearing on long-term corrosion or radionuclide release rates from glasses. The only significant effect identified in the literature that is attributed to alkali ion exchange is an increase in solution pH in static laboratory tests conducted at high surface area-to-volume ratios (Strachan et al. 1990; Bourcier and Feng 1993).

The discovery of the significance of ion exchange to long-term radionuclide release rates was only very recently made possible by the development of computational tools that can simulate the coupled processes of glass dissolution, mass transport, and chemical reactions in a complex disposal system (Chen, McGrail, and Engel 1997). By comparing simulations where Na ion exchange was included versus those where it was excluded, Chen, McGrail, and Engel (1997) showed that the ion-exchange reaction increased the pH in a conceptual design for a LAW disposal vault from approximately 9.8 to over 12.5, which increased the radionuclide release rate by over 3 orders of magnitude. Thus, the overall performance of the disposal system can be significantly improved if improved glasses are developed that minimize alkali ion exchange. Formulation of such glasses can be rationally accomplished only through development of a fundamental scientific understanding of the ion-exchange process. Such a study is currently being supported under DOE's Environmental Management Science Program (EMSP), and the results and conclusions from this work will be closely coordinated with the testing program described in this report.

3.2 Glass Corrosion Model

It is impossible to develop a rationale testing program without thoroughly understanding the model that is being used to calculate the glass corrosion behavior over the geologic time scales required for performance assessment. In fact, the testing program is directly linked and derived from the data requirements of this model. Figure 3-1 illustrates the basic linkage between modeling and testing. At the top of the pyramid is the conceptual model that describes the glass corrosion process. The parameters that make up this model are abstracted at the mid-level of the pyramid. Once the parameter set is known, the testing program is determined by the appropriate experiments needed to obtain each parameter in the set. This strategy is consistent with American Society for Testing and Materials guidelines (ASTM 1991), but we emphasize the "model driven" approach here because, ultimately, the credibility of the performance assessment rests on the credibility of the models and supporting data, not on a specific test. Following this approach, the conceptual model for glass corrosion planned for use in the performance assessment is discussed in the next section.

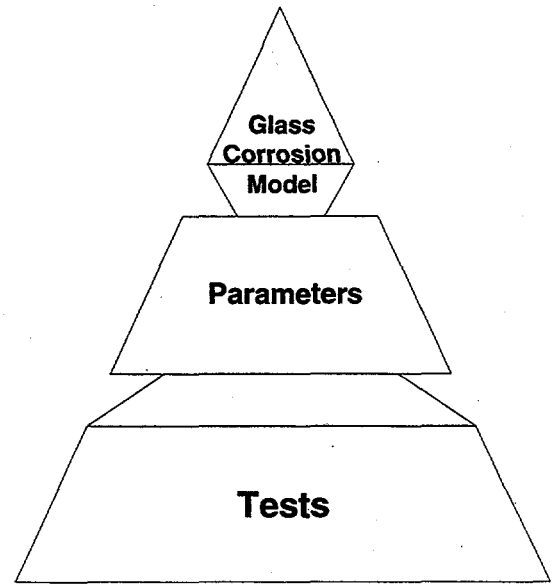

Figure 3.1. "Top-Down" Strategy for LAW Glass Testing

3.2.1 Rate Law for Hydrolysis and Dissolution

The literature on modeling glass dissolution is extensive. However, Strachan, Bourcier, and McGrail (Strachan et al.1994) published a recent review of the subject. An interested reader should consult this paper and the references cited therein for additional details. The conclusion from this study was that of all the models that have been developed to describe glass dissolution behavior, the general kinetic rate law proposed by Aagaard and Helgeson (Aagaard and Helgeson 1982) and later adapted by Grambow (Grambow 1985), best describes the majority of the experimental data that has been gathered over 35 years of studying glass/water reaction processes. Consequently, this model has been selected for use on the LAW disposal project. The corrosion of silicate glasses in water can be represented as a special type of irreversible dissolution reaction. The reaction is irreversible because the glass cannot be reformed by precipitation from aqueous solution.

A conventional transition state kinetic rate equation can be used to compute the flux of any element i released from the glass into the aqueous phase and is given by

$$J_i^a = \nu_i \bar{k} e^{-\frac{E_a}{RT}} \left[1 - \left(\frac{Q}{K} \right)^{\sigma} \right] \prod_j a_j^{-\eta_j}, \quad i = 1, 2, \ldots N; \; j = 1, 2, \ldots M \tag{1}$$

where

a_j = activity of jth aqueous species

$\bar{k}$ = intrinsic rate constant, $g/m^2 \cdot s$

E_a = activation energy, J/mol

J_i^a = flux of element i to the aqueous phase, $g/m^2 \cdot s$

K = equilibrium constant of rate controlling reaction

M = number of species directly affecting the rate

N = number of elements

Q = ion-activity product of rate controlling reaction

R = gas constant, 8.314 J/mol·K

T = temperature, K

ν_i = stoichiometric coefficient of element i in the glass

σ = net reaction order

η_j = stoichiometric coefficient for the jth reactant species.

Equation (1) is a constitutive relationship that relates temperature and the composition of water contacting the glass to the corrosion rate. Currently, H^+ is the only aqueous species that has been found to directly influence the rate via the activity product term (Bourcier et al. 1992). Consequently, Equation (1) can be simplified to

$$J_i^a = \nu_i \bar{k} e^{-\frac{E_a}{RT}} a_{H^+}^{-\eta} \left[1 - \left(\frac{Q}{K} \right)^{\sigma} \right], \quad i = 1, 2, \ldots N \tag{2}$$

where a_{H^+} is the hydrogen ion activity. Because the temperature is assumed to be a known constant, and ν_i values are determined from the glass composition, application of Equation (2) for modeling glass corrosion in a disposal system requires the determination of six parameters; $\bar{k}$, E_a, η, σ, K, and Q. In accordance with the strategy illustrated in Figure 3.1 and the ASTM 1174 approach, the testing program is then defined by an appropriate set of experiments that determines these parameters.

3.2.1.1 Experiments for Kinetic Rate Law Parameters

If a glass is placed in a dilute solution that is refreshed at an infinite rate, the chemical affinity term $[1-(Q/K)^{\sigma}]$ in Equation (2) equals 1, and the corrosion rate of the glass is determined only by the three traditional kinetic rate law parameters, $\bar{k}$, E_a, and η. Experimentally, the single-pass flow-through (SPFT) test is used to approximate these conditions. By adjusting glass surface area and flow rate, the solution remains dilute, but not so dilute that the solution concentrations cannot be determined with standard analytical techniques. The SPFT test has been used to measure reaction rates of minerals (Knauss and Wolery 1986; Dove and Crerar 1990) and glasses (Knauss et al. 1990; McGrail and Olson 1992; McGrail et al. 1997c). By monitoring the change in dissolution rate over a sufficient range of temperature and pH values, $\bar{k}$, E_a, and η can be easily obtained by applying standard nonlinear regression techniques to Equation (2). Details of the recommended experimental procedure and tests are given in Section 4.1.

3.2.1.2 Experiments for Affinity Term Parameters

By definition, σ and K are the *parameters* of the chemical affinity term $[1-(Q/K)^{\sigma}]$ and so are usually obtained from laboratory experiments. The ion activity product (Q) is a *variable* and must be computed as a function of time and space for the disposal system (McGrail and Mahoney 1995; Bacon and McGrail 1997). Computation of Q is complex and depends on physical properties of the system, such as flow rate and glass surface area, and chemical properties, such as solubility products and the amounts and types of alteration products formed (see Section 3.1.1). Because transport and chemical processes interact, or more precisely are coupled, a special type of computational model, called a reactive chemical transport model, is required for simulations.[a] The key inputs to this model derived from the glass testing program are the parameters σ and K, and the identification of glass alteration products. These data are extremely important because they can affect the calculated long-term corrosion rate of the glass by 3 to 4 orders of magnitude.

The pseudoequilibrium constant (K) and reaction order parameter (σ) are probably the most difficult parameters to obtain in the rate law, and, unfortunately, are also the most poorly documented in terms of experimental techniques and methods for obtaining them. Unlike for a crystalline or amorphous phase, the assignment of K for a glass is ambiguous, because by definition, equilibrium between the glass and water does not exist. Assigning K to a hypothetical phase including all the glass elements has not proven successful in modeling laboratory test data (Bourcier 1989; Advocat et al. 1990). Consequently, an approximation is used where K is associated with a reversible microscopic reaction that is rate limiting and not the macroscopic glass/water reaction itself. Good agreement with laboratory test data for most glasses has been obtained by assigning K to a simple SiO_2 polymorph, such as chalcedony, or mixtures of simple hydroxides and silicate phases (Bourcier et al. 1990; Gin 1996).

Unfortunately, the "agreement" typically reported in the literature lacks a statistical basis and is usually just trial and error reckoning of batch test data to calculated curves (Bourcier et al. 1990). The situation for determining the parameter σ is even poorer with most studies of silicate mineral and glass dissolution simply assuming $\sigma=1$. In other cases (Bourcier et al. 1994), σ and/or K have been regressed using data from batch tests. Batch tests introduce additional difficulties in accurately obtaining these parameters because pH and solution concentrations change continuously throughout the test, requiring "corrections" derived from the rate law itself. This introduces the possibility of inseparable causality errors. In a recent paper, McGrail et al. (1997c) illustrated how the SPFT test can be used to obtain σ and K by varying the flow rate over a sufficiently wide range. Their technique has the advantage of being performed at fixed pH and steady-state solution concentrations and does not require data "corrections" derived from the rate law. Consequently, the experimental techniques and formal mathematics developed by McGrail et al. will be used to obtain these parameters (see Section 4.1).

Because there is no single test that can reliably evaluate the effects of secondary phases on the long-term corrosion rate of a glass, our approach is to employ a range of accelerated experimental techniques. By doing so, a range of physical and environmental factors can be

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[a]The interested reader should consult McGrail and Mahoney (1995), Chen et al. (1997), and Bacon and McGrail (1997) for details.

examined that affect the rate and type of secondary phases formed. The use of different tests to accelerate glass corrosion provides added confidence that the artifacts associated with each test method are understood and properly taken into account and that long-term corrosion behavior of the glass is understood. Three types of long-term experiments are recommended for the majority of the testing: 1) vapor hydration tests, 2) product consistency tests (PCTs), and 3) pressurized unsaturated flow (PUF) tests. Each of these tests, and alternative tests, are discussed in detail in Section 4.0.

3.2.2 Rate Law for Ion Exchange

Although ion exchange has been largely ignored in the recent literature on the glass/water reactions, the process has been the subject of numerous early studies. In fact, the traditional idea of glass "leaching" involves the basic mechanism of ion exchange in which an H^+ or H_3O^+ ion exchanges for an alkali ion (M^+) in the glass, thereby generating a hydrated layer on the glass surface. The overall chemical reaction describing the process can be written as:

$$\equiv\text{Si-O-M} + H^+ \rightarrow \equiv\text{Si-OH} + M^+ \tag{3}$$

or

$$\equiv\text{Si-O-M} + H_3O^+ \rightarrow \equiv\text{Si-OH} + M^+ + H_2O. \tag{4}$$

Rana and Douglas (Rana and Douglas 1961a and 1961b) were among the first to report on this mechanism. Boksay, Bouquet, and Dobos (Boksay 1968) and Doremus (Doremus 1975; Doremus 1977; Lanford et al. 1979) pioneered the idea that ion counter-diffusion or interdiffusion is the rate limiting process for the exchange reaction. Recent data on a representative LAW glass, LD6-5412, is also consistent with a diffusion-controlled release mechanism. Figure 3.2 shows that Na is being released, presumably by ion exchange, at a linear rate with respect to $t^{1/2}$ in excess of the rate of matrix dissolution.

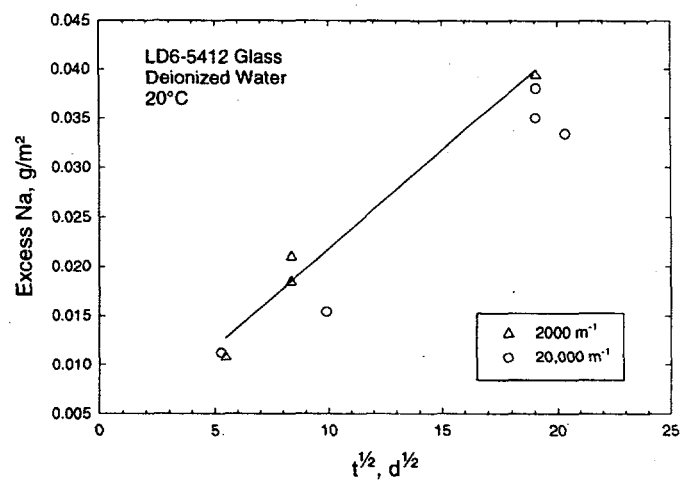

Figure 3.2. Release of Na in Excess of that Released by Matrix Dissolution in Static Tests with LD6-5412, a Reference LAW Glass

Detailed studies of the ion exchange process(es) are being conducted under the EMSP program. Once these studies are complete, an appropriate rate equation for ion exchange will be developed. The parameters that make up this model (possibly diffusion coefficients) will need to be determined from laboratory tests on the vendor glass compositions. However, until the EMSP studies are further along, it is premature to identify specific test methods and conditions.

4.0 Laboratory Testing

Waste glasses are laboratory tested to identify important corrosion processes under site-relevant conditions and to measure parameter values needed to model long-term behavior (see Section 3.0). Three general classes of tests are proposed in this strategy: 1) characterization, 2) accelerated, and 3) service condition. Characterization tests are used isolate and provide specific information about processes or parameters in theoretical models. Test conditions are usually very different from expected service conditions to highlight a particular process and minimize or hold constant other effects. Examples of such tests include measuring basic material properties, such as density and compressive strength. Characterization tests proposed in this plan related to glass corrosion are SPFT tests used to measure kinetic rate law parameters.

Accelerated tests are used to investigate corrosion behavior that will be important over the regulated service life of a disposal system within a laboratory time frame of a few years or less. Therefore, it is important to know likely site conditions over long times to determine what aspects of glass corrosion need to be considered in the performance assessment. Elevated temperatures and high glass surface area-to-solution volume ratio (S/V) are often used to accelerate the reactions and processes that lead to glass dissolution. It is important to verify that the technique used to accelerate a reaction or process does not cause a change in the rate-limiting step or mechanism of the process, or if it does, the change must be taken into account. For example, water diffusion, ion exchange, and hydrolysis will be affected to a different degree by changes in the temperature, and the overall temperature dependence of glass corrosion will include contributions from all three processes, although it may be dominated by one process under particular test conditions. Accelerated test methods that will be used to study the advanced stages of glass dissolution include the PCT, the vapor hydration test (VHT), and the PUF test. Tests will be conducted over a range of conditions to link the dissolution behavior under disposal conditions with that under accelerating test conditions.

Service condition tests are conducted to verify that the techniques used in accelerated tests do not change the alteration mechanisms. They are designed to approximate, to the extent possible in the laboratory, the physical and chemical environment of the disposal system. Because of the low temperature of ILAW disposal system and the very slow rate of moisture flow expected in the disposal facility, laboratory tests approximating these conditions are unlikely to yield meaningful data in reasonable time periods. Consequently, no specific service condition tests are proposed in this plan. Rather, the parameter values for some tests are selected so as to reflect service conditions. For example, some PUF experiments may be performed with fractured glass monoliths instead of ground glass to provide service condition information on water flow paths and glass alteration processes in fractures. However, solution flow rate and temperature adopted for these tests will likely be higher than the expected conditions. Again, the purpose of the testing program is to demonstrate a scientific understanding of the processes controlling long-term glass corrosion so that the *models* describing these processes can be used with confidence in extrapolating to the expected service conditions.

Having described the general types of tests to be performed, the specific characterization and accelerated tests proposed under this plan are discussed in Sections 4.1 through 4.9.

4.1 Single-Pass Flow-Through Test

The SPFT test is an open system test where a solution at a known flow rate and constant temperature flows through a reaction cell that contains the sample. The configuration precludes recirculation of a portion of the effluent and so makes a "single-pass" through the reaction cell. Many different SPFT apparatuses have been developed, but these can all be classified as three basic types: 1) well-mixed batch, 2) packed bed, and 3) fluidized bed. The advantages and disadvantages of each design are discussed below.

4.1.1 Well-mixed Batch Reactor

Figure 4.1 shows a schematic of a typical batch flow through cell. Fluid and, optionally, a gas or gas mixture is pumped into the cell. Fluid exits the cell and is collected in a separate container for later chemical analysis. Mixing is accomplished by convection from the solution flow and (optionally) gas flow into the reactor. Some researchers have used a mechanical stirrer as well. The key advantages to using this type of reactor include the ability to use powdered or monolithic samples, use and control a gas or gas mixture during the test, and eliminate the need to control bubble formation in the fluid inlet, as is necessary with a packed bed reactor (see below). The only disadvantage to using a batch reactor is the need to ensure that when using powdered samples, sufficient mixing occurs to prevent agglomeration of the particles or formation of a stagnant solution around the sample.

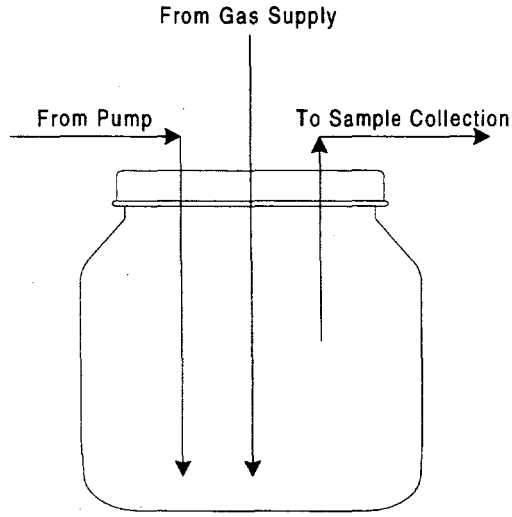

Figure 4.1. Schematic of Batch Flow-Through Reactor

4.1.2 Packed Bed Reactor

Figure 4.2 shows a schematic of a typical packed-bed type reactor. A porous bed of the test material is packed between two frits that have a nominal pore size smaller than the particle size of the sample. Solution flows through the porous bed and is collected in the same manner as with the batch reactor. The key advantage to using this type of reactor is that it eliminates the possibility of a stagnant solution layer as is possible with a batch reactor. However, this design has several important disadvantages. Care must be exercised to ensure that gas bubbles do not form in the inlet lines, which can become entrained in the porous bed. Entrained bubbles could exclude part of the sample surface from contact with the fluid. McGrail and Olson (1992) reported that it was impossible to prevent bubble formation in their fluid inlet lines at 90°C, despite vigorous attempts to degas the solution. This limited the effective operating temperature to 70°C or less. The second disadvantage is that by the nature of the design, a concentration gradient will exist across the bed. However, depending on the specifics of the corrosion mechanism, this may or may not be of concern. Finally, the option of imposing a fixed gas partial pressure in the reaction cell is not available as with the batch type of reactor.

4.1.3 Fluidized Bed Reactor

Figure 4.2. Schematic of Packed Bed Reactor

The fluidized bed reactor is similar to the packed bed reactor except that much less sample is used so that when sufficiently high flow rates are used, the sample particles are suspended or "fluidized" in the cell. The advantages of this design are that it eliminates the concentration gradient inherent with the packed bed reactor and ensures complete exposure of the entire particle surface area to the fluid. However, this test configuration has numerous disadvantages. First, depending on the particle size and density difference between the sample and the fluid, a relatively high flow rate is required to fluidize the bed. The flow rate required can often be sufficiently high that the solution exiting the reactor does not differ enough from background concentrations to be statistically significant. This is particularly problematic at lower temperatures because the flow rate required to fluidize the bed will change only slightly with temperature, but the dissolution rate of the test material may decrease by 2 to 3 orders of magnitude over the temperature range of 90 to 20°C, thus compounding detection limit problems. Second, the high flow rates required generate large volumes of effluent. This can present an expensive waste disposal problem, especially when testing radioactive materials. Third, because the particles are in motion and collide with one another, particle abrasion may cause a change in surface area during the test, which may be difficult to quantify. Fourth, the reactor must be carefully engineered and tested to prevent particles from settling in quiescent pockets and from transporting out of the reactor to the collection system.

4.1.4 SPFT Testing Strategy

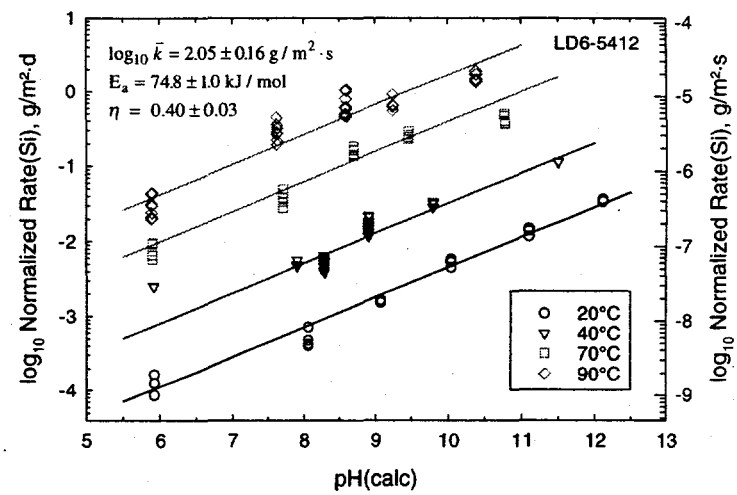

Figure 4.3. Normalized Si Release Rate as a Function of pH and Temperature for LD6-5412 Glass

Based on the discussion of SPFT testing methods in Sections 4.1.1 through 4.1.3, the advantages of the batch reactor are sufficient to select it as the preferred test apparatus design. Testing must then be performed over an appropriate range of conditions. The pH of the water percolating through a LAW disposal system will almost certainly be between pH 6 and 13, so the pH dependence of the rate must be determined over this range. Collecting SPFT data over the acidic pH range is not required. The activation energy (E_a) is another important parameter in the model, and SPFT tests must be run over a sufficient range of temperatures to accurately determine this parameter. A typical data set that provides the three parameters, $\bar{k}$, E_a, and η, is shown in Figure 4.3.

The procedures outlined in McGrail et al. (1997c) should also be followed in running SPFT tests over a sufficient range of flow rates to evaluate the parameters σ and K. Although K should be independent of pH and perhaps σ as well, at least one additional experiment at another pH should be performed for confirmation. Finally, test results (McGrail et al. 1997c) on LD6-5412 glass indicated the possibility that an additional element (besides Si), such as Al, may need to be included in the affinity term. If a similar conclusion is reached based on the SPFT test results for the vendor glass compositions, then a series of tests should be performed where the concentrations of the test element(s) are varied independently. An analytical solution for a mixed Si-Al kinetic rate law model was developed by McGrail et al. (1997c) and can be used to develop a statistical design for these tests.

4.2 Vapor Hydration Test

The VHT is the simplest accelerated test to be used in the recommended testing strategy because there is only one degree of freedom in test parameters that can be varied, temperature, excluding test duration and humidity. The principle use of the test is as a convenient means of generating alteration phases for analysis within a short period, but it is also useful for a qualitative measure of the effect of alteration phase formation on the corrosion rate. The VHT is a static test in which a monolithic sample is exposed to water vapor in a sealed vessel, as illustrated in Figure 4.4. At relative humidity (RH) above about 80%, a thin film of water condenses on the sample. The thickness of the film increases with the RH, and it is in this film that the glass corrodes. The thickness of the film determines the effective S/V ratio of the system; for a uniform layer, the S/V ratio is simply the inverse of the thickness of the film. Most VHTs have been performed in 100% relative humidity at temperatures above 100°C, although tests have been conducted at lower humidities and temperatures. At the completion of a test, the sample is removed from the vessel, and the reacted surface is analyzed with high-resolution electron microscopy. Discrete precipitated crystalline phases usually form when the sample corrodes. The solution evaporates from the sample when the test is terminated and is not available for analysis. This precludes using the test to evaluate and test models of glass corrosion behavior, which require detailed measurements of the solution composition in contact with the glass.

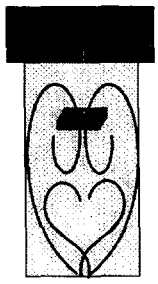

Figure 4.4. Schematic of VHT

Vapor hydration has been used by archaeologists to replicate the weathering observed on obsidian artifacts recovered from terrestrial sites (Friedman and Long 1976). The method has also been used to simulate the long-term weathering of tektite (Mazer et al. 1992) and basaltic glasses (Byers et al. 1986). Because the test method produces the same alteration phases that form during the weathering of natural glasses over long periods, the test has also been used to accelerate the corrosion of waste glasses. High-level waste glasses commonly form clay layers in VHTs. Glasses having compositions relevant to anticipated LAW for Hanford form zeolite phases similar to analcime, gobbinsite, and phillipsite.

To extract kinetic information, VHTs will be run over a minimum of four temperatures, all at 100% RH. However, it is important to recognize that the rate measured in VHTs is not the glass dissolution rate, but the rate at which alteration phases are formed. It is presumed that

precipitation rates of the alteration phases are much faster than the glass dissolution rate. Tests with radioactive glasses will be used to measure the distribution of radionuclides between alteration phases and residual phases (see Section 4.6).

4.3 Product Consistency Test

The PCT has been standardized as an ASTM standard procedure (ASTM 1994). The ASTM standard includes two methods: PCT Method A was developed specifically for verifying process control of vitrified HLW forms and is conducted with specific values of test parameters; PCT Method B does not specify the values of test parameters. Because the PCT Method B encompasses commonly used variations of test parameters, we refer to all static dissolution tests with crushed glass generically as PCTs.

The PCTs are conducted by reacting an aliquot of crushed glass that has been sieved to isolate the desired size fraction with an aliquot of a solution in a sealed vessel at the desired temperature. The glass S/V can be calculated from the glass/solution mass ratio and the specific surface area of the crushed glass to determine the average dissolution rate during the test. Tests are conducted as batch tests wherein a separate test is run for each duration. At the end of the test, the solution is analyzed for pH and the concentrations of dissolved glass components. The latter are used to calculate the amount of glass that has reacted and the dissolution rate. The reacted glass surface can also be analyzed to help characterize the reaction mechanism, such as when an alkali-depleted layer or alteration phases form.

Because the test conditions in PCTs are water-saturated and static (closed-system), which are not consistent with expected disposal system conditions, including a significant number of PCTs in this plan requires explanation. Traditionally, PCTs are used as a means to study advanced stages of corrosion at high glass/solution mass ratio (or S/V), high temperature, and long test duration. It is argued that the reaction conditions in the PCTs are similar in several regards to the conditions expected in a disposal site. Although waste glasses will not be crushed, the S/V values commonly used in PCTs are similar to the effective S/V values when a small volume of water contacts a glass. The static conditions of the PCTs are also probably not too different from the very low water infiltration rates anticipated. Therefore, PCTs probably provide a fair simulation of the corrosion behavior after a small amount of water has contacted a waste package and reveal key reaction processes. While each of these statements is true to some extent, they provide insufficient justification for running PCTs as they establish only heuristic connections with modeling.

Consistent with the model-centered approach used in this plan, the PCT is used to calibrate the substantial set of supporting geochemical data that are required for modeling the dynamic evolution in solution chemistry that occurs as a consequence of glass/water reactions. The term "calibration" in this context refers to a complex iterative process whereby the evolution in solution composition and secondary phase formation observed in PCTs is reproduced, with a reasonable level of uncertainty, in a geochemical model of the system. The process is complex because during a closed-system test, like the PCT, changes in the concentrations of dissolved glass components, the solution pH, and, in some cases, dissolved air components must be modeled simultaneously. Fortunately, the geochemical simulator selected for modeling this

system, the EQ3/6 code (Wolery and Daveler 1992), has capabilities for handling these complexities.

The calibration process requires, among other things, estimating solubility product values for secondary minerals that are identified in the PCTs, but for which thermodynamic data are not available. These values can be generated by fitting to the PCT data or by using empirical methods, such as with a polymer model (Mattigod and McGrail 1998). However, if a particular phase is found to have an important effect on long-term glass corrosion rates, it is recommended that independent measurements of its solubility product be performed. Once the geochemical model has been calibrated against the PCT data, the significant aqueous speciation and dissolution-precipitation reactions in the model can be identified. This reaction set and supporting thermodynamic data then make up the reaction network that is used in the reactive transport model to compute radionuclide release from the disposal system (Bacon and McGrail 1997).

Because the dissolution behavior of glasses in PCTs are usually strongly affected by the affinity term, PCT results can also be used to measure of the values of the saturation concentration (K) and the net reaction order variable (σ). However, the effect of a changing pH and solution composition complicates the extraction of these values. Instead, the results of PCTs conducted for long durations can be used to confirm the values of K and σ that are derived from the SPFT tests (see Section 4.1).

There are two degrees of freedom for parameter variation in PCTs, temperature and S/V, excluding test duration. It is recommended that PCTs be performed at a minimum of four separate temperatures between 20 and 90°C and at two S/V ratios. Tests at elevated temperatures are needed to measure the trends in the corrosion behavior as a function of temperature and to determine if the corrosion mechanism changes with temperature. Use of higher S/V ratios provides another means of accelerating the extent of reaction. However, there are limits to the values of S/V that are practicable. At S/V ratios >20,000 m^{-1}, test artifacts become important. Initial alkali ion exchange and dissolution of fines can increase leachate ionic strength and pH to values that are unrealistic for a disposal system subject to open-system mass transport. In PCTs conducted in containers impermeable to air, the available $CO_2(g)$ can also be consumed, which compounds the pH excursion from the ion-exchange and limits the formation of important carbonate minerals. Consumption of water from hydrolysis of the glass becomes an important consideration, as the S/V could be a steeply time-varying function. This makes interpretation of the test data much more difficult. Consequently, it is recommended that the S/V be limited to a maximum of 20,000 m^{-1}.

4.4 Pressurized Unsaturated Flow Test

The PUF test is a new technique developed at PNNL for testing waste forms (McGrail et al. 1997a and 1997b). The experimental design provides a novel way to study waste form corrosion behavior under unsaturated conditions, subject to open-system flow and transport. Like the SPFT test, the PUF test provides three degrees of freedom for parameter variation: temperature, glass surface area, and flow rate.

The basic test apparatus consists of a column packed with glass particles (or other material) of a known size and density, and a computer data acquisition and control system (see Figure 4.5). The column is fabricated from a chemically inert material so that dissolution reactions are not influenced by interaction with the column. A porous titanium plate of proprietary design is sealed in the bottom of the column to ensure an adequate pressure differential for the conductance of fluid while operating under unsaturated conditions (Wierenga et al. 1993). Titanium was chosen because it is highly corrosion resistant and has excellent wetting properties. When water saturated, the porous plate allows water but not air to flow through it, as long as the applied pressure differential does not exceed the air entry relief pressure or "bubble pressure" of the plate. The computer control system runs LabVIEW™ (National Instruments Corporation) software for logging test data to disk from several thermocouples, pressure sensors, inline sensors for effluent pH and conductivity, and column weight from an electronic balance to accurately track water mass balance and saturation level.

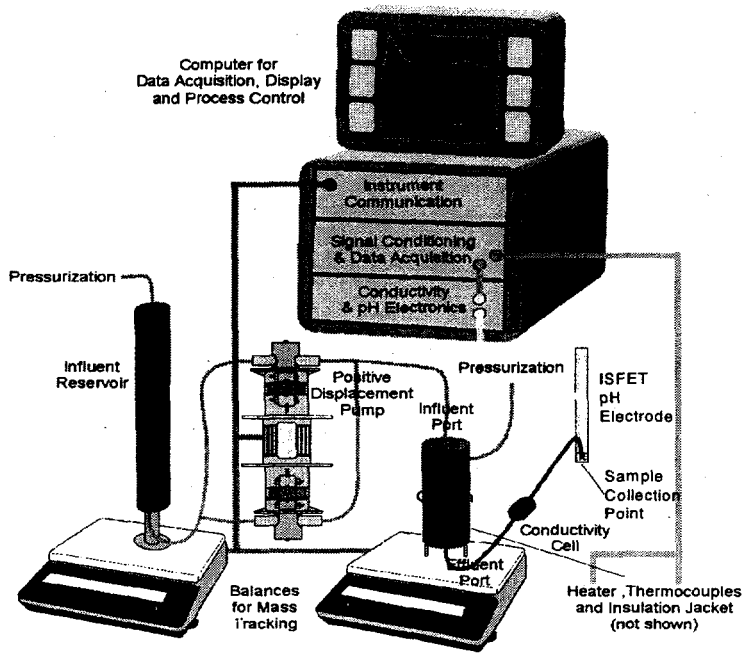

Figure 4.5. Schematic of PUF Apparatus[(a)]

Several important findings have resulted from PUF experiments that have been performed on LD6-5412 glass and SRL-202 glass, a reference HLW glass for the Defense Waste Processing Facility. With LD6-5412 glass, precipitation of zeolitic secondary phases was correlated with an acceleration of the glass reaction rate, exactly as was found in PCTs conducted at a high surface area-to-volume ratio (S/V) of 20,000 m^{-1} and the same 90°C temperature. However, in the PCTs, the accelerated reaction stage did not occur before about 120 to 240 days. In the PUF test, the accelerated reaction stage was reached after only about 12 days. This is an acceleration factor of about 10 to 20, even though the specific surface area of the glass used in the PUF test was about 10 times smaller than the specific surface area of the glass used in the PCTs. In the PUF test with SRL-202 glass, precipitation of an alkali aluminosilicate phase (currently being identified), was correlated with a 50% decrease in volumetric water content, indicating a change in the hydraulic properties of the sample. This is this first evidence ever reported that corrosion and secondary phase precipitation can induce changes in the unsaturated hydraulic properties of a glass waste form. Experiments with Pu-containing glass packed in a thin layer between two layers of SRL-202 glass (not containing Pu) have also shown that >90% of the Pu, brought into solution from corrosion of the Pu glass, exits the column as a colloid. This is important because to exit the column as a colloid in this experiment, the colloids must have been transported approximately half the column length through a layer of crushed SRL-202 glass. Consequently,

[(a)]Patent pending

the PUF test provides a means to study the formation and transport of radiocolloids under unsaturated flow conditions.

Based on the findings from the PUF experiments that have been run to date, the test will play an important role in the overall testing strategy. First, because the test combines glass corrosion, unsaturated flow, and mass transport processes under controlled conditions, it is ideally suited to provide data for validation of the reactive transport model being used for long-term performance calculations for the disposal system (Bacon and McGrail 1997). Second, the demonstrated ability to accelerate the transformation of the glass into alteration products means that the test will provide critical information on these phases, and the stability of the glass with respect to the formation of these phases, in relatively short periods of time. Third, aged samples from the test can be independently evaluated for changes in unsaturated hydraulic properties, thereby providing critical data for modeling fluid flow through the disposal system. Fourth, the flow-through configuration allows for different engineered-barrier materials to be tested in combination to evaluate interactive effects on glass corrosion rates and/or radionuclide release (see Section 4.7).

Although the PUF test is assigned a key role in the overall testing strategy for the ILAW program, it must be recognized that because of the complex apparatus required, the number of PUF experiments that can be performed is constrained by relatively high costs per test, equipment availability, and access to skilled technicians to run the test. Consequently, it is recommended that PUF tests be performed at three different temperatures only. Also, because very little information currently exists on the effect of flow rate on the PUF test results, a series of tests should be performed on one vendor glass formulation that covers a range of flow rates. These experiments should be designed to examine whether the corrosion rates can be correlated with a reduced parameter, such as the ratio of volumetric flow rate to glass surface area, a well-defined correlating parameter in SPFT tests (McGrail et al. 1997c). Finally, tests are recommended with radioactive glasses (see Section 4.6) and a series of materials interaction experiments with at least cement and glass combinations, but perhaps including iron or iron corrosion products as well (see Section 4.7).

4.5 Other Test Methods

Other test methods have been used to measure the values of model parameters and to study glass corrosion behavior under site-relevant conditions. Some of the more commonly used test methods are described below. The reasons why these tests are not included in the testing strategy for Hanford LAW are also discussed. Basically, the other test methods described below provide little or no additional relevant information when compared with the tests proposed in Sections 4.1 through 4.4.

4.5.1 Soxhlet Tests

Soxhlet tests provide a method for measuring the glass corrosion rates under highly dilute conditions. Soxhlet tests are performed by reacting a sample with condensed fluid in a refluxing apparatus. Water is boiled from a reservoir, condensed in a reflux tube, then allowed to drip into a small cup that contains the sample. The solution in the sample cup is refreshed as condensate drips into the sample cup. Complete volume replacement of the fluid in the cup typically occurs

every few minutes but the precise replenishment time depends on the sample cup volume and refluxing conditions. The refluxing action provides an effective flow rate that can be varied by controlling the applied heat flux to the device. Tests are usually run to attain a flow rate sufficiently high that the solution in the sample cup remains highly dilute. The corrosion rate can be measured by periodically removing a sample of the solution in the reservoir for analysis. The Materials Characterization Center Soxhlet test (MCC-5) specifies the use of a monolithic sample and an all-Teflon apparatus (Strachan et al. 1981), although crushed samples and stainless steel apparatuses have also been used.

Soxhlet tests have been utilized to measure the initial corrosion rate of glasses as a function of the temperature, particularly for European HLW glasses (Delage and Dussossoy 1991; Tovena et al. 1994). Unfortunately, because the system operates with condensed vapor, the dissolution rate can only be easily measured at the pH of distilled water at the test temperature. Because the dissolution rate is required over a pH range of 6 to 13, the SPFT technique (see Section 4.1) is preferred for these measurements.

4.5.2 MCC-1 Test

The MCC-1 static leach test method was developed to compare the durabilities of candidate waste forms developed to stabilize high-level nuclear wastes (DOE 1982). The test procedure has been standardized by the ASTM (ASTM 1992). The method calls for placing a monolithic specimen of known geometric surface area into a volume of solution such that the S/V is 10 m^{-1}. The test may be performed with demineralized water, a reference silicate solution, or a reference brine. The reference temperature and time are 90°C and 28 days, although temperatures of 40 or 70°C and other durations can be used.[a] The MCC-1 test typically provides a solution-dominated system in that the leachate remains dilute as the glass dissolves. However, tests conducted for long time periods may be affected by changes in solution chemistry. Samples corroded in MCC-1 tests show details of the chemical and physical alteration of the glass surface and have provided insight into mechanisms controlling the initial stages of corrosion (Bates et al. 1991; Oversby and Phinney 1992).

While the MCC-1 method was originally designed to compare the relative chemical durabilities of candidate waste forms, the test can be used to characterize several aspects of the corrosion process in conjunction with a corrosion mechanism. Tests conducted for short time periods provide a simple means of measuring the glass corrosion rate under dilute conditions. Tests have been performed in buffer solutions or solutions spiked with various glass components to determine the effects of the leachate chemistry on the glass corrosion rate (Advocat et al. 1991). Longer term tests can be run to monitor the alteration of the glass surface during corrosion to investigate the corrosion mechanism (Strachan 1983; Bates et al. 1991). However, because each of these processes is covered in greater depth using SPFT and PCTs, there is no compelling need to include MCC-1 tests in the testing strategy for LAW glass.

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[a]The MCC-2 test procedure is a variation of the MCC-1 procedure that permits reaction temperatures of 110, 150, and 190°C.

4.5.3 MCC-3 Solubility Test

The MCC-3 test was designed to measure the maximum solubility of a waste form in the solution of interest (MCC 1984). This test method formed the basis of the PCT. Tests were to be conducted until the solution composition did not vary with the reaction time (i.e., until the glass "saturated" the solution). However, application (Shade and Strachan 1986) of the test method showed that 1) constant solution compositions were not achieved within a few weeks, and 2) the solution composition depended on the particle size of the glass used. The first observation is a direct result of the glass reactivity, while the second is due to the different S/V that results from the different total surface areas of different sieve fractions. Tests conducted at higher S/Vs usually generate more concentrated solutions. The MCC-3 procedure was subsequently modified such that 1) a single size fraction is specified, and 2) the test vessel is continuously agitated during the test, usually by placing the vessel on a roller. The PCT has effectively replaced the MCC-3 test in most laboratories, although all of the complications associated with the use of crushed glass found during development of the MCC-3 tests are common to the PCT procedure.

4.5.4 Periodic Replenishment Tests

Several test methods have been developed in which leachate solution is periodically removed from an ongoing static test and replaced with an equal volume of fresh solution. Such replacement tests have been used to simulate very low flow rates that cannot be attained using mechanical pumps (Barkatt et al. 1983 and 1984). Either monolithic or crushed samples can be used, and different starting solution compositions can be used. Specific test methods have different replacement schedules and replace different fractions of the total solution volume. For example, the test designated by the International Standardization Organization (ISO) calls for replacing the entire solution volume daily for the first week, every week for eight weeks, monthly for six months, and twice yearly thereafter (Hespe 1971). The American Nuclear Society test method ANS 16.1 and variations of the ANS 16.1, such as the Dynamic Leach Test (DLT) and the Accelerated Leach Test (ALT), are similar total volume exchange tests. They differ primarily in the replacement schedules. These tests were developed to characterize materials from which contaminants are assumed, a priori, to be released by a diffusion-controlled process, such as with grouts and cements. Although the ANS 16.1 test is required for LAW in the Phase 1 Hanford Privatization Contracts, this type of test provides little insight to the long-term corrosion behavior of glass waste forms. This is because concentrations of the waste form components and solution pH change over time in the fluid contacting the waste form until the fresh fluid is injected, which then causes a sudden and abrupt change in the solution chemistry. Such conditions are extremely difficult to interpret and cannot be treated adequately with conventional geochemical computer codes. Consequently, no periodic replenishment tests are proposed in this plan.

4.5.5 Unsaturated or "Drip" Test

The Unsaturated Test or "drip test" was developed at ANL to simulate the corrosion of a waste glass that is intermittently contacted by transient water in an unsaturated geologic environment, such as that at Yucca Mountain (Bates and Gerding 1986). A sample of the waste form and possibly other engineering or geologic materials is placed in the center of a reaction

cell. A small amount of liquid water is injected through a septum and allowed to drip from the feed tube onto the upper surface of the sample. Initial aliquots of added water are vaporized until the air is saturated; subsequent aliquots drip onto the sample. Solution that drips from the sample during the test and collects in the bottom of the test vessel can be analyzed to quantify the amount of glass that has dissolved and been transported away from the waste form. The corroded glass can also be analyzed to assess the corrosion mechanism, study materials interactions, and identify any alteration phases that form (Woodland et al. 1991). Unsaturated tests are being used as one of the primary sources of radionuclide release data in a total system performance assessment for the Yucca Mountain Site (Stout and Leider 1996).

Unfortunately, the "drip test" has several drawbacks with respect to evaluating LAW glass behavior relevant to disposal at the Hanford Site. First, the drip test is a quasi-static method, similar to the periodic replenishment tests discussed in Section 4.5.4. Consequently, the same difficulties exist in applying conventional modeling tools for modeling the experiment as were previously described for these tests. Second, the exact amount of fluid in contact with the sample at any given time is not known (and likely variable), so the effective S/V, a key parameter needed in modeling, is poorly defined. Finally, the drip test was originally designed as a service condition test corresponding to a particular scenario at the Yucca Mountain Site where fluid may periodically drip on the waste packages from fluid-filled fractures. This "drip" scenario does not represent a possible hydrodynamic condition for the ILAW disposal system, which is located in a shallow, sandy soil. The PUF method is preferred for unsaturated testing because it applies a steady unsaturated hydraulic condition on the sample, and the total amount of water in contact with the sample is continuously monitored.[a] These features make the PUF test amenable to modeling using standard computational methods and tools.

4.5.6 Accelerated Dissolution Test

The accelerated dissolution test (ADT) was designed to measure the dissolution rate of a glass in the presence of its alteration phases and in a solution that is in near equilibrium with those phases. The alteration phases are generated by vapor hydration of a sample of the glass being evaluated, and the nearly saturated solution is generated in a PCT conducted at high S/V and at the temperature at which the dissolution rate is to be measured. The dissolution rate is measured by mass loss of a fresh monolithic sample. To date, the ADT has only been applied to measure the dissolution rate of the LD6-5412 glass (Ebert et al. 1996). The rate measured with ADTs was consistent with that estimated from long-term PCTs and that extrapolated from VHTs. However, an inoculation period existed in which the dissolution rate was at first very low and then increased because of the effects of the alteration phases. The occurrence of this period, which was of different durations in replicate tests, is not fully understood, but may be related to time needed for the solution and alteration phases to equilibrate. A specific role for the ADT has not been identified in this plan, but the test will likely continue to be used periodically to confirm long-term dissolution rates measured in VHTs and PCTs.

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[a]The capability to monitor spatial variations in moisture distribution during a PUF test will be available shortly at PNNL with the installation of an X-ray computed microtomography system.

4.6 Required Tests with Radioactive Glasses

In Sections 4.1 through 4.5, no distinction was made with regards to testing "cold" or fully radioactive glasses. Because the ultimate goal of the testing program is to evaluate long-term radionuclide release rates, and not glass corrosion rates per se, some testing must obviously be performed with radionuclide-containing materials. However, it is not required that all testing be performed with radioactive materials. This is because the radionuclides found to be of most concern in the performance assessment (Mann et al. 1998) for the LAW disposal system are ^{99}Tc, ^{79}Se, and ^{129}I. These radionuclides are extremely soluble under the oxidizing conditions that are expected at the site. Consequently, the rate of glass corrosion ultimately determines the rate of release for these important elements. However, at very long times, Pu and U isotopes also contribute to the computed doses from the groundwater pathway (Mann et al. 1998). These elements are expected to form sparingly soluble precipitates in the disposal vault and may also be transported as colloids, so the release rates will not depend directly on the corrosion rate of the glass. For these elements, experiments with radioactive glasses are needed to identify the solubility-controlling phases. Release rates of the soluble radionuclides also need to be checked for congruency with the rate of glass corrosion to eliminate the possibility of a mechanism, such as ion exchange, that could selectively enhance release rates.

Because only very limited data have been obtained with a single LAW glass (LD6-5412) doped with ^{99}Tc, it is difficult at this time to define what amount of testing with radioactive glasses is required. The level of testing also depends strongly on future funding levels for the LAW disposal program. A reasonable conjecture includes a reduced set of VHT, PCT, and PUF tests with a fully radioactive glass containing each radionuclide of interest. The reduced set may include VHTs at one temperature, PCTs at two temperatures but only the highest S/V, and PUF experiments, also at two temperatures, but at two flow rates and one glass surface area. Concentrations of the radionuclides in the test glasses likely should not reflect the expected activity levels in the actual glass product. Consideration should be given to doping the test glasses at significantly higher levels than expected so that it is easier to identify secondary solids containing the radionuclides. Because the radionuclide concentrations and radioactivity levels of LAW glass are very low, there is little or no concern regarding radiolysis-induced experimental artifacts or having the radioactive glasses exhibit different long-term corrosion behavior when compared with nonradioactive glasses.

4.7 Materials Interaction Tests

The LAW disposal system will include the following additional materials, besides glass, that are used in construction or as part of the waste package: 1) concrete used in the vault walls, ceiling, and floor; 2) carbon or stainless steel containers used to hold the glass; and 3) filler material used inside the containers to consume void space. Of these materials, the concrete is of the most interest because of the anticipated volume required, approximately 320,000 metric tons (Burbank 1997), and the chemical effect of the concrete in increasing pH and Ca, Na, and K concentrations. Corrosion of the metal containers will generate iron oxyhydroxides that are known to adsorb or coprecipitate with Si (Harder 1978). This can act as an additional sink for Si, resulting in enhanced rates of glass corrosion (McVay and Buckwalter 1983; McGrail 1986). However, iron hydroxide precipitates may also have a beneficial effect in that they are well

known adsorbents for a wide variety of metals, and so could lower release rates for some radionuclides. No specific filler material has been identified, so the significance of this material to glass corrosion behavior cannot be assessed at this time.

Because the concrete is used exclusively on the exterior of the vaults, the interactive effects of the concrete on the glass (if any) will most likely be confined to a region at the "interface" between the two materials. This is because diffusion and/or advection limit the total mass flux of OH^-, Ca^{2+}, etc. from the concrete that is available for reaction with the glass. To properly test this mass transport rate limited process in the laboratory, a technique is required where mass transport by diffusion and/or advection from the concrete into the glass can be controlled. Batch experimental methods, such as the VHT or PCT, are intentionally designed to be well-mixed systems to avoid mass transport constraints on the reaction processes. Consequently, these methods are unsuited for this materials interaction study. Fortunately, the PUF technique provides a means to control mass transfer and transport rates by the particle size and flow rate used in the test. The concrete and glass can be configured sequentially, such that the water can "equilibrate" with the concrete before entering the porous glass bed. By comparing differences in corrosion rates and radionuclide release, with and without the concrete, and by examining the alteration products formed, especially at the interface between the two materials, a good understanding of the interactions between the materials can be developed.

Interactive effects with the container or iron corrosion products are more difficult to assess because the material will be distributed throughout the disposal system, including the interior region of each vault. In this case, the mass transport limitations discussed above for the concrete do not apply, at least on a scale larger than a single waste package. A highly localized assessment of the interactive effect could be obtained by running a VHT where the container material and glass are "sandwiched" together. An alternative would be to run PCT or PUF experiments where the glass and container material particles are mixed together in volume percentages equivalent to what is expected in the current disposal system design. Glass corrosion rates would then be directly compared with and without the metal present to obtain a direct assessment of the interactive effects, if any. Care must be exercised in these tests to ensure that the available O_2 is not consumed from oxidation of the steel.

4.8 Role of Natural Analogs

Analogy is a scientific method that uses inference from certain resemblances to imply a probable further similarity (Ewing and Jercinovic 1987; Petit 1992). The term natural analog refers to a material or process that resembles those expected in a waste disposal system or the methodology used to study and assess them. The analysis of analog materials has been used to enhance confidence in the validity of long-term predictions made with mechanistic models, as well as assisting in the development of those models (ASTM 1991). By studying the alteration of natural materials that has occurred over millions of years due to weathering in a range of terrestrial environments, insight has been gained into the long-term corrosion behavior of waste glasses in a disposal environment. This is done by characterizing the natural alteration of the analog material and comparing it to alteration produced in laboratory tests with naturally occurring or chemically identical synthetic materials. In addition to studying the natural alteration of a material, it is also important to identify the alteration mode(s) that controls

corrosion of the analog material and to verify that the same process that controls the rate in the short-term testing also controls the long-term behavior that is being modeled. Applications of natural analogs include

- comparing alteration products generated during long-term corrosion of natural glasses to those generated in accelerated laboratory tests to verify experimental methods of accelerating glass corrosion
- studying specific reaction processes that are important in waste glass corrosion and are highlighted in the corrosion mechanism of a natural material
- studying the relationship between the kinetics of natural glass corrosion measured in short-term laboratory tests and the known long-term durability of the glass to verify that the appropriate reactions and processes are modeled for long-term calculations
- calibrating the degree to which a laboratory test accelerates a corrosion mode.

The use of natural analogs to extract kinetic information is usually limited to bounding estimates because of the uncertain and changing conditions to which the analog material has been subjected, including wet/dry cycling, variations in temperature and water composition, etc., and uncertainty regarding the age of the sample itself. In most cases, kinetic information must be extracted by examining reacted solids that are usually incomplete assemblages of alteration phases. Nevertheless, corroded natural glasses provide valuable insight regarding corrosion processes that are important to long-term corrosion and confidence in the accelerating properties of laboratory tests.

Geologists have studied samples of basaltic glasses recovered from marine, geothermal, and subglacial environments. Corrosion of basaltic glasses results in the formation of palagonite, which is a generic term for an assemblage of alteration phases that includes clays and zeolites. The same phases have been observed to form in nature and in laboratory tests (Lutze 1985; Byers et al. 1985). In both natural settings and in laboratory tests, the amounts and in some cases the identities of phases that are formed depend both on the glass composition and the environmental conditions (e.g., the temperature, chemistry, and volume of the solution contacting the glass). Waste glasses have been shown to react similarly to basalt glasses in laboratory tests and to transform to many of the same phases. This provides evidence that 1) the laboratory test accelerates the corrosion behavior of basalt glasses and leads to the same phases formed in nature over very long time periods and 2) the same processes that control long-term basalt glass corrosion in terrestrial sites (and under terrestrial conditions) also control the long-term corrosion of waste glasses.

Long-term testing of natural analog glasses using VHT and PCT methods is being funded at ANL through separate DOE programs. Consequently, there are no current plans to support additional VHT and PCT testing of natural analogs through the ILAW disposal project. However, the PUF method has only recently been developed, and no natural materials have been examined using this test method. Consequently, a small number of long-term PUF tests should be performed using a selected natural analog. The preferred material would have a much higher alkali content than is typical of rhyolitic or basaltic glasses and would have been subjected to environmental weathering conditions analogous to those expected for the disposal system. One possible site for such samples is the obsidian flows at Newberry Crater, Oregon (25 miles south of Bend, Oregon), which range in age from 1,200 to about 6,700 years B.P. This area has an arid

environment similar to that of the Hanford Site and potentially provides similar analogs at different ages within a short distance of each other. Regardless, the selected natural analog sample for study must be as well-characterized as possible in terms of the sample age and weathering conditions if it is to be useful for comparing against data from PUF experiments.

4.9 Laboratory Testing Strategy Summary

Table 4.1 represents a compilation of the recommended testing discussed in Sections 4.1 through 4.6. To the best of the authors' current knowledge, this is the minimum matrix of laboratory tests required to fully characterize the long-term corrosion and radionuclide release behavior of a glass waste form for disposal at the Hanford Site. A duration limit of 2000 days was selected because the major decisions regarding acceptable glass compositions and disposal system design need to be made in approximately the next 5 years. Consequently, tests beyond this time frame will have little impact on the overall program.

A key issue not discussed in the strategy up to this point is variability. Variability in the waste stream delivered to the private vendors will result in variability in the composition of the glass product; i.e., no single glass composition represents the entire inventory of glasses to be produced during the vitrification campaigns. Glass compositional variability must also be addressed in evaluating the long-term performance of the disposal system. One approach is to identify a selected set of glasses that represent compositional extremes and then perform a reduced set of experiments on these glasses. The results from these tests can then be used to bound the release rate behavior for entire compositional space. Once data are available on the reference vendor glass compositions and the variability expected during processing is quantified, specific compositions and tests can be proposed.

Table 4.1. Master Test Matrix for Long Term Performance Evaluation of a Glass

Test Method	Temp	pH	Flow Rate	Surf. Area	Sol. Vol.	Duration Range (days)
SPFT($\bar{k}$, E_a, η)	4	6	Var.[1]	1		14-30
SPFT(K, σ)	1	2	15	1		14-30
VHT	4					1-2000
PCT	4			2[2]	1[2]	30-2000
PUF	3		3	2		30-2000
Rad. Glasses						
VHT	1					1-365
PCT	2			1[2]	1[2]	30-2000
PUF	2		2	1		30-2000

[1]Flow rate sufficiently high so that $Q/K \approx 0$.
[2]Varied as S/V.

5.0 Field Testing

Field testing provides a unique opportunity to obtain site-relevant data on the corrosion behavior of waste forms under conditions that more closely approximate service conditions than is possible in the laboratory. Recognizing this fact, several burial studies with glass waste forms have been conducted in the United States and abroad. One of the first studies involving glasses was carried out in the early 1980s at the Stripa Site in Sweden. The Stripa Site is an abandoned iron mine located in a granitic formation approximately 350 m below the surface. Specimens were fabricated in a "pineapple slice" geometry and stacked into assemblies that were either heated to 90°C or maintained at ambient mine temperatures (8 to 10°C). Samples were extracted at predetermined intervals (0.25, 0.5, 1, and 2 years) for extensive characterization using surface spectroscopic and microscopic analytical techniques. In the United States, a comprehensive field test involving HLW glasses was performed for the Materials Interface Interaction Tests (MIITs) at the Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico. Located approximately 650 m below the surface in the Salvo salt formation, a wide array of glasses and waste package materials were tested for 5 years. Pineapple slices of test samples were stacked on heated Teflon assemblies in such a manner as to test a variety of interfacial reactions. The United States also has participated in burial studies conducted at the Mol Site in Belgium (clay geology) and Ballidon Site in the United Kingdom (limestone) in an effort to test the performance of a simulated HLW glass (SRL-165) in other geologies.

At the Hanford Site, grout waste forms have been field tested in lysimeters at the Grout Waste Test Facility located in the 300 Area (Last et al. 1995). A lysimeter essentially consists of a corrugated steel container buried flush with the ground surface. Lysimeters can range in size from small soil-filled cans, a few centimeters in diameter and a few centimeters deep, to large caissons that are several meters wide and tens of meters deep. Lysimeters can be simply designed with little or no peripheral instrumentation, or they can be designed with extensive monitoring features, including devices for monitoring temperature, water content and matric potential and devices for extracting samples of water for chemical analysis. Lysimeters have been built and used at the Hanford Site for a variety of reasons, including the assessment of recharge rates, biointrusion studies, radionuclide transport studies, evapotranspiration studies, and field-scale waste-form performance tests (Gee and Jones 1985; Rockhold et al. 1995).

Although lysimeters have several disadvantages, they are a logical choice for field testing of the glass corrosion and contaminant transport models being developed for the ILAW disposal system. The devices provide a way to combine a LAW glass, Hanford soil, and perhaps other engineered materials in a well-controlled test but on a scale that is not practicable in the laboratory. The test is controlled because the walls of the lysimeter form a physical boundary in the system being studied that defines a fixed volume for calculating water storage and tracer mass balance and restricting the geometry of flow within the lysimeter to essentially one dimension. Interpretation of complex temporal variations in tracer release and transport is much simpler in one spatial dimension. The field scale affords the opportunity to monitor contaminant release and transport in time and space that is not possible in laboratory experiments, such as with the PUF test (see Section 4.4). This is especially true when operating under low moisture content conditions where the volume of solution available per cubic meter for collection of samples is small.

Lysimeter experiments should be used as a tool to confirm the coupled glass corrosion and contaminant transport model described in Section 3.0. For this purpose, there is no need to exclusively test glasses similar in composition to the vendor's formulation or to simulate natural conditions as much as possible. Instead, some experiments should be run with an applied steady flow rate of water and with a glass designed to have high corrosion rate so that it is easier to monitor contaminant release and transport during the test. It is also important that these experiments be designed and instrumented appropriately so that data can be collected to support validation studies of other key models being used on the ILAW disposal program, such as a multiphase flow simulator.

6.0 Modeling the Disposal System

The previous discussion of the testing strategy would not be complete without a discussion of the linkage to modeling the disposal system, as this is the ultimate use of the data generated by the testing program. The fundamental objective of the performance assessment for disposing of LAW is to calculate the radiation dose to a future population as a result of any release and transport of radionuclides to the unconfined aquifer located approximately 70 m below the disposal facility. Computer models will be used to simulate the processes controlling the release and transport of radionuclides to the unconfined aquifer. The computer codes must perform three major simulation functions: 1) release of contaminants from the vitrified waste, 2) transport of those contaminants through the engineered system, and 3) transport through the vadose zone to the groundwater. In Section 3.2.1, we presented the kinetic rate law for glass corrosion:

$$J_i^a = \nu_i \vec{k} e^{-\frac{E_a}{RT}} \left[1 - \left(\frac{Q}{K} \right)^{\sigma} \right] \prod_j a_j^{-\eta_j}, \quad i = 1, 2, \ldots N;\ j = 1, 2, \ldots M. \tag{1}$$

Assuming that $\vec{k}$, E_a, η, K, and σ are all known parameters developed from the laboratory testing program, to determine the mass flux of any component i released from the glass to the aqueous phase, it is necessary to calculate the pH and ion activity product, Q. Because the calculation of these chemical variables depends on both the physical properties of the system, such as flow rate and glass surface area, and chemical properties, such as solubility products and the amounts and types of alteration products formed, functions (1) and (2) discussed above cannot be decoupled. A special type of computational model, called a reactive chemical transport model, is required for simulations.

In 1995, the Hanford Low-Activity Waste Disposal Project selected a reactive transport code to calculate contaminant release rates from the engineered components of the disposal system (McGrail and Mahoney 1995). The **A**nalyzer of **R**adionuclid**E** **S**ource **T**erm with **C**hemical **T**ransport (AREST-CT) code describes multicomponent reactive transport in an isothermal, partially saturated, porous medium. The model includes chemical reactions between aqueous, gaseous, and solid phases. Reactions involving minerals are described through appropriate kinetic rate laws, along with a special option for treating irreversible reactions (such as glass corrosion) via the kinetic rate, Equation (2). Homogeneous reactions within the aqueous phase are assumed to be reversible with their reaction rates controlled by transport and local equilibrium mass action relations. Local equilibrium between a gas or gas mixture and the aqueous phase is treated through Henry's law. Solute transport includes contributions from advection, diffusion, dispersion, and radioactive decay.

Because of evidence from PUF experiments that significant changes in hydraulic properties may occur as a result of precipitation of secondary phases, it was decided in 1997 to incorporate a multiphase flow and transport capability into AREST-CT so that these property changes could be coupled to the flow field. The specific mechanisms incorporated in the code are changes in porosity, and hence hydraulic conductivity, caused by mineral precipitation/dissolution and changes in water saturation caused by water consumption/production in chemical reactions. This was accomplished by coupling AREST-CT with STOMP, a nonisothermal, multiphase flow

simulator (White and Oostrom 1996). The new coupled code is called STORM, Subsurface Transport Over Reactive Multiphases.

As it is currently configured, the STORM code represents a relatively complete model of the physical and reactive chemical transport processes that are required for simulating radionuclide release rates from the disposal system. However, several improvements to the code are needed to support long-term performance calculations, especially in more than one spatial dimension. These improvements can be classified in terms of 1) subprocess models and 2) numerical methods.

6.1 Subprocess Model Development

STORM has two subprocess models requiring further development: 1) adaptive reaction network and 2) composition-dependent hydraulic property model.

6.1.1 Adaptive Reaction Network

The set of reactions to be considered in a single STORM run, the reaction network, is fixed as specified in the input file. Consequently, careful consideration must be given to including all important solid and solution species that may be important in the system. This is extremely difficult because the system being modeled is usually changing chemically in time and space, often in ways that cannot be predicted a priori. Consequently, solid and solution species that were important at the start of a run can become unimportant components in the reaction network and vice versa. A subprocess model is needed in STORM that adapts the reaction network periodically. This can be accomplished by conducting a phase boundary search at each node. The phase boundary search is a numerical implementation of the mineralogic phase rule. It operates by querying a general thermodynamic database and computing an ion activity product for each solid that could exist in the current system based on the elements being considered. Supersaturated phases are added to the reaction network, and undersaturated phases can be deleted. However, because the dissolution rate of a phase is finite, deletion of the phase from the network is constrained until the total mass falls below some specified value.

6.1.2 Composition-Dependent Hydraulic Property Model

Unsaturated flow experiments with glass waste forms have shown that the dissolution of the glass and subsequent formation of secondary minerals, such as zeolites and clays, can change the unsaturated flow properties of the glass (McGrail et al. 1997c.). Constitutive equations are used in computational modeling of multiphase flow to relate changes in flow properties, such as hydraulic conductivity and permeability, to changes in primary variables, such as matric potential or volumetric water content (Tietje and Tapkenhinrichs 1993). For example, a water-retention function developed by van Genuchten (1980) is commonly used in modeling unsaturated flow in porous media

$$\theta = \theta_r + (\theta_s - \theta_r)/[1+(\alpha\psi)^n]^m \qquad (5)$$

where θ, θ_r, and θ_s are water content, residual water content, and saturated water content, respectively, ψ is matric potential, and α, n, and m are fitted parameters that are related to the

physical properties of the porous medium. Physical properties, such as porosity, tortuosity, air entry matric potential, residual moisture content, etc., are typically assumed as invariant properties of the matrix, and so α, n, and m are assumed to be constant as well. Such assumptions are invalid in chemically reactive systems where macroscopic changes in physical and chemical properties can be induced by interphase mass transfer reactions that affect the pore scale. In general, the most important mass-transfer reactions involve dissolution of primary solid phases and concomitant precipitation of secondary solid phases.

A fundamental physicochemical basis for modifying the empirical fitting coefficients used in constitutive relationships, like the van Genuchten function, for multiphase flow through a system containing fractured glass should be developed. One possible approach to develop an appropriate model is to conduct experiments where hydraulic and physicochemical property data are obtained on uncorroded and corroded glass samples, possibly obtained from PCT and PUF experiments. This data set will form the basis for developing physicochemical constitutive relationships for unsaturated flow. These relationships can then be tested by comparing computer simulations with measurements of the solid phase and moisture distribution during PUF tests (see Section 4.4).

6.2 Numerical Methods

The vitrified waste may be in the form of large glass blocks riddled with stress fractures. Berkowitz, Bear, and Braester (1988) suggested that solute transport in fractured media can be considered at a number of different scales. A near-field scale would include a few discrete fractures near the source. At a far-field scale, the fractured media could be treated as a continuum that is representative of an equivalent porous medium in which the repeating fractures behave as large pores. Their work focused on a contaminant source surrounded by a fractured porous medium. The fractured glass waste packages emplaced in a vault (Figure 2.1) presents a different situation; the contaminants are already distributed within the glass matrix and are released as the glass dissolves. Given the low flow rates through the vault, the contaminants will be mixed by diffusion within each fracture. If stress fractures in the glass waste form are numerous and closely spaced, a continuum approach to modeling flow and transport through the vault will likely be adequate. Consequently, developing a model capable of handling flow and transport in discrete fractures is not warranted at this time.

Currently, STORM executes on a fixed, 2-D cartesian finite grid. This makes the code inefficient when handling sharp concentration fronts that commonly develop in reactive transport simulations. Consequently, implementing an adaptive gridding algorithm is recommended. Adaptive gridding provides a means to increase the number of computational cells in regions where sharp concentration fronts exist and coarsens the grid where concentrations are uniform. This refinement better captures the movement of these fronts with less numerical dispersion and increases execution speed by putting extra grids at only those locations where they are needed.

Two-dimensional simulations of coupled unsaturated flow and reactive transport with STORM require significant computing resources. A two-dimensional simulation with 22 aqueous species, 9 solid species, 10 equilibrium reactions, and 10 kinetic reactions on a 30 by 35 grid requires 1 week to reach a simulation time of 20,000 years running on a Sun Ultra 1. A

sensitivity analysis consisting of multiple two-dimensional runs would therefore take years to complete.

Several alternatives exist for decreasing the execution time of the code. The simplest is to execute the simulations on a workstation with a faster scalar central processing unit (CPU). Workstations are available that are several times faster than a Sun Ultra 1; within 5 years, workstations will be available that are 10 to 100 times faster than a Sun Ultra 1. A second alternative is to adapt STORM for execution on a machine with multiple, parallel processors. Currently, an effort is underway at PNNL to develop a parallel multiphase flow and reactive transport code, targeted for execution on an IBM NWMPP1 computer, capable of 247 GFLOPS. However, the reactive transport algorithm used in this code, operator-splitting, is likely to be restricted to much smaller time steps than the global-implicit algorithm used in STORM. Once this new code is available, testing will be performed to determine the relative efficiency of two codes in running an actual LAW disposal system simulation. If significant improvements in execution time are demonstrated on a realistic simulation, then the techniques and algorithms developed from the research program on parallel multiphase flow and reactive transport codes may be implemented in a parallel version of the STORM code so that it may be used to solve the larger problems required for the LAW disposal system performance assessment.

6.3 Disposal System Simulations for the Performance Assessment

The ultimate objective of the laboratory and field testing, and model development activities discussed in the previous sections of this report is to provide technically credible calculations of radionuclide release and transport in support of a formal performance assessment for the ILAW disposal system. The general methodology (Mann et al. 1998) is to divide the problem into logical parts that correspond to the computer simulation tools that will be applied in different parts of the problem domain. Figure 6.1 illustrates the recommended overall computational strategy. The very-near-surface infiltration rate provides a key boundary condition for the remainder of the simulations. The coupled unsaturated flow, chemical reactions, and contaminant transport simulator (see Section 6.0) is applied from just below the root zone to some distance into the soil (probably several meters) below the floor of the disposal vault. This region is defined as the near field. Water exiting the region near the vault is expected to be of high ionic strength and pH and this plume will migrate down into the soil column for some distance until dispersion and chemical interactions with the soil components attenuate it. Beyond this depth, the chemical composition of the migrating fluid will likely change very little. Consequently, it is possible to limit the domain over which computationally intensive reactive chemical transport simulations must be performed by switching to a chemically non-reactive vadose zone flow and transport simulation in the far-field domain. The radionuclide flux exiting the vadose zone to the unconfined aquifer is computed with this model and is used as a boundary condition for the unconfined aquifer flow and transport simulator. The final step in the methodology is to compute the impacts, if any, from ingestion, inhalation, and external radiation to humans who become exposed to the contaminants by withdrawing water from the aquifer and using it for drinking, farming, and other purposes.

The methodology outlined in Figure 6.1 is remarkably robust for conducting a performance assessment. Each simulation tool is based on basic principles of physics, chemistry, and thermodynamics. No ad hoc assumptions are made about the performance of the waste form or other components of the engineered and natural system. Consequently, changes in boundary conditions, such as infiltration rate, or scenarios, such as an assumed failure of the capillary break, can be quantitatively assessed in terms of their overall impacts on system performance. Of course, the database needed to support the mechanistic models used in the selected simulation tools is substantial. In this report, we have attempted to define the minimum required data set to support the coupled unsaturated flow, chemical reactions, and contaminant transport simulator (see Section 4.0). Although a considerable amount of testing is required, it is not intractable. Similar statements can be made about the other parts of the methodology. Consequently, the approach outlined in Figure 6.1, and especially the laboratory and field testing required to support it, are not unreasonable or unrealistic, assuming current programmatic funding levels and schedule are maintained.

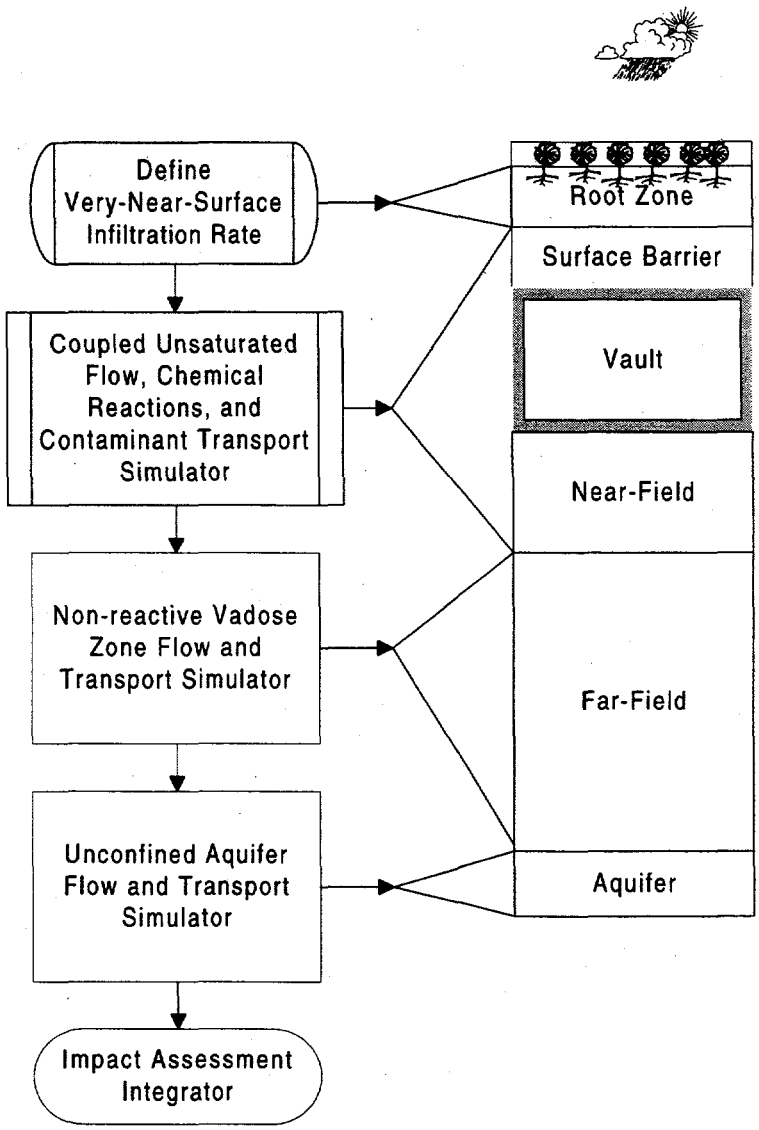

Figure 6.1. Modeling Strategy for Assessing ILAW Disposal System Impacts

7.0 Conclusion

An overall strategy for evaluating the long-term performance of a low-activity waste glass at Hanford has been presented. The strategy combines laboratory testing and field testing into an overall plan for demonstrating a scientific understanding of the processes controlling long-term glass corrosion. Models describing these processes can then be used with confidence in extrapolating to the disposal system conditions and calculating radionuclide release rates in a formal performance assessment.

The recommended laboratory testing includes single-pass flow-through (SPFT), product consistency (PCT), and pressurized unsaturated flow (PUF) tests. The majority of the laboratory testing (~80%) is to be conducted using nonradioactive glasses, with the remainder performed with glasses containing a selected set of key radionuclides. Additionally, a series of PUF experiments with a natural analog of basaltic glass are recommended to confirm that the alteration products observed under accelerated conditions in the PUF tests are similar to those found associated with the natural analog. This will provide additional confidence in using the PUF test results to infer long-term corrosion behavior.

The final component of the strategy is a set of field experiments using both vendor glasses and specially formulated highly reactive glasses. The purpose of these experiments is to validate the models for glass corrosion and reactive chemical transport that form the technical basis for calculating radionuclide release rates in the disposal system. These experiments can be performed in existing lysimeters at the Hanford Site, or in new lysimeters that have been equipped with the latest in monitoring equipment and located near the proposed disposal site. The field tests will be closely coordinated with other tasks on the ILAW, so that may serve to validate other key model inputs to the performance assessment.

8.0 References

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