Glass Leaching Performance

L. A. Chick
R. P. Turcotte

May 1983

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I. SUMMARY

This report summarizes current understanding of the leaching performance of high-level nuclear waste (HLW) glass. The review evaluates performance with respect to all major variables. It discusses general behavior using an empirical model which emphasizes the effect of water flow rate on glass leach rate. The model identifies the special importance of silicon solubility as a constraint on leaching kinetics. A report by Schneider et al. (1982) uses some of the information presented here to estimate repository performance relative to safety criteria. The primary function of the present report was to provide a cohesive data base from which these and more detailed analyses could be undertaken.

The empirical model of waste glass leaching behavior developed shows that at high water flow rates the glass leach rate is kinetically limited to a maximum value. At intermediate water flow rates, leaching is limited by the solution concentration of silica and decreases with decreasing water flow rates. Release of soluble elements is controlled by silica dissolution because silica forms the binding network of the glass. At low water flow rates, mass loss rates reach values controlled by formation rates of alteration minerals, or by diffusion of dissolution products through essentially stagnant water.

The parameters reviewed with respect to their quantifiable influence on leaching behavior include temperature, pH, leachant composition, glass composition, thermal history, and radiation. Of these, temperature is most important since the rate of mass loss approximately doubles with each 10°C increase in dilute solutions. The pH has small effects within the 4 - 10 range. The chemical composition of the leachant is most important with regard to its influence on alteration product formation. Glass composition exhibits the largest effects at

high flow rates where improved glasses leach from ten to thirty times slower than glass 76-68. The effects of the thermal history (devitrification) of the glass are not likely to be significant. Radiation effects are important primarily in that radiolysis can potentially drive pH values to less than 4. Radiation damage to the glass causes insignificant changes in leaching performance.

Use of the laboratory data to estimate representative leach rates involved making important assumptions in five areas. These include:

- 1) Contact by water occurs at $T < 100^{\circ}\text{C}$.
- 2) The pH of the repository water remains between about 4 and 10 and does not have a strong influence on bulk leach rate.
- 3) The effective normal repository water flow rates will be low enough that glass leach rates will be controlled by silicon concentrations in solution, by diffusion in the leachant, or by alteration product formation rates.
- 4) At low flow rates, release rates of more soluble elements can still be up to a factor of ten higher than that of silicon; sodium is a good indicator.
- 5) Alteration product formation rates probably present the largest uncertainties in predicting glass release under repository conditions. However even the most soluble radionuclides can be released no faster than the kinetically limited leach rate of the glass.

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II. INTRODUCTION

A. Background and Purpose

In late fiscal year 1982, the U.S. Department of Energy (DOE) formally separated nuclear waste management R&D related to the commercial fuel cycle from that associated with defense wastes. The Commercial Waste Treatment Program (CWTP) was created at PNL to establish licensable technologies for treating the high-level and transuranic portion of these commercial wastes. An early goal of this program is to establish waste form performance requirements and summarize existing waste form performance information. Then by comparing information about the needed and the expected performance, technically-based decisions can be made about the adequacy of waste forms. The purpose of this document is to summarize existing laboratory leaching data, combine it in a form useful to estimate glass performance in a repository environment, and discuss the magnitude and nature of the uncertainties implicit in making performance estimates. A companion document, "The Adequacy of Borosilicate Glass as a Form for Commercial High-Level Waste" by Schneider et al. (1982) provides the performance requirements and an assessment of the ability of borosilicate glass to meet those requirements in all parts of the waste management system.

In recent years, waste form leaching performance has become the characteristic of primary concern. An intensive comparative evaluation of alternative waste form properties and processes for disposal of defense nuclear wastes led to the choice of borosilicate glass as the defense waste form and included development of a waste form-product performance hierarchy in which all relevant properties were considered and weighted in terms of perceived importance. In that evaluation (Gordon et al. 1982), leach performance was valued at 73% of the total figure of merit. At the same time, a national Nuclear Waste Materials Characterization Center was established at PNL (1979) to standardize performance test methods. The work undertaken during FY 1983 within the MCC focuses almost entirely on leach performance evaluation,

particularly emphasizing test methods simulating geologic environments. Within the NWTS and its predecessor organizations, a generic effort has been in progress for approximately ten years to select a repository site. Four geologies were identified -- salt, basalt, tuff and granite -- for intensive evaluation. With respect to the waste form, these programs emphasize leach performance exclusively, limited to studies of borosilicate glasses and spent fuel. To summarize, there is a national consensus that the predominant waste form characteristic of importance to repository disposal is the leach performance. For these reasons, this review focuses on leach performance of waste glasses for commercial nuclear wastes.

B. Waste Glass Development/Compositions

It is well known that there are a wide variety of waste compositions which have been incorporated in glass. For economic reasons, high waste loadings (25 to 35 wt%) have been emphasized, hence different glass compositions have been developed for different specific wastes. Table I shows a selection of HLW glasses developed throughout the world. Figures 1a and 1b summarize the range of glass compositions tested in glass development studies in the United States and in Japan. Other countries have performed similar studies. It is evident that a wide variety of compositions have been studied, although many of the compositions chosen as reference glasses are borosilicates similar to PNL 76-68 glass.

Some of the variation in HLW glass compositions can be attributed to the wide variation in waste compositions. However, since the waste usually comprises 1/4 to 1/3 of the glass, most of the glass composition is at the discretion of the developer. The developer chooses glass forming additives which yield a workable compromise between product and process properties. Desirable product properties include a low leach rate and little tendency to devitrify. Processing properties include the temperature dependence of viscosity, volatility, and

TABLE 1. Commercial HLW Glasses from the U.S.A. and Other Countries (wt%)

Frit	USA(a) 76-68	USA(a) 77-260	France(b) LWR	Sweden(c) ABS-39	Japan(d) POS77	Germany(e) 98-20
SiO ₂	40.0	36.0	47.5	48.5	47.5	40.2
B ₂ O ₃	9.5	9.0	15.0	19.1	13.5	10.8
Na ₂ O	7.5(12.5)(i)	8.0(11.1)(i)	12.0	12.9	2.0(9.4)(i)	21.9
ZnO	5.0	--	--	--	1.0	--
CaO	2.0	1.0	4.0	--	1.0	2.2
K ₂ O	--	2.0	--	--	1.0	--
TiO ₂	3.0	6.0	--	--	--	3.3
Al ₂ O ₃	--	2.0	3.0	3.1	2.5	1.1
CuO	--	3.0	--	--	--	--
Li ₂ O	--	--	--	--	2.0	--
BaO	--	--	--	--	1.0	--
<u>Waste</u>	(f)	(g)				
Fe ₂ O ₃	9.64	(h)	5.0	5.7	--	1.87
Na ₂ O	4.98	3.13	--	--	7.4	--
Gd ₂ O ₃	--	9.84	--	--	--	--
Other Inerts	1.08	3.97	0.5	--	8.4	0.82
Fission Products	12.71	10.99	13.0	9.0	12.9	16.64
Actinides	4.59	5.25	(j)	1.66	--	1.07

(a) Ross, et al. 1978.

(b) Sombret, 1982.

(c) KBS, 1981.

(d) K. Ishiguro, private communication.

(e) Walker and Riege, 1979.

(f) PW-8a.

(g) PW-7c.

(h) Included in "other inerts".

(i) Total Na₂O in waste plus frit.

(j) Included with "fission products".

Figure 1a. Ternary diagram of glass formers, modifiers and inter-mediate, showing nuclear waste glass composition experimental region (from Chick et al. 1981)

Figure 1b. Composition region for waste glass development study in Japan (from K. Ishiguro, Power Reactor and Nuclear Fuel Development Corporation, Japan)

electrical conductivity. For the PNL-developed joule-heated continuous electric melter, the viscosity of the glass should be near 100 poise and the electrical conductivity between 0.2 and 0.5 (ohm-cm)⁻¹ at the 1150°C processing temperature. The PNL waste glass used in generating most of the available leaching data (76-68) was developed in 1976 for the in-can melting process which required a 100 poise viscosity at 1050°C. The CWTP is now developing commercial waste glasses for the continuous electric melting process. These updated compositions can be expected to have somewhat improved leach rates due partially to increased understanding of the effects of composition on leaching behavior and partially to the 100°C higher melting temperature which will require less alkali metal oxides in the compositions. In spite of this increased understanding, there are as yet no simple explanations for the rather broad range of leach rates which have been reported for different glasses. Detailed studies of 76-68 glass therefore can be extrapolated to other compositions only with some caution. It should also be recognized that different versions of the basic 76-68 composition have been distributed through the years for testing. These different samples can produce leaching results differing by at least a factor of two. Differences also exist in the test methods which have been utilized by various laboratories. Thus, even for leaching data restricted to 76-68 glass, we should expect to see some considerable variation.

III. WASTE GLASS LEACHING

Large research efforts have been underway for several years studying the many aspects of leaching of waste glasses. Although the leaching process is still not completely understood, laboratory data collected under an increasing diversity of experimental conditions is available. Plodinec et al. (1982) summarized leaching data and assessed defense waste glass performance using a different approach than is used

herein. The main limitation to confidently use laboratory data to predict the long-term leaching of glasses in a repository is that most of the laboratory experiments have been run for less than a year under simplified, nonradioactive conditions, while the predictions must be valid for much longer periods under complex repository conditions. Better understanding of leaching mechanisms and waste package-geology interactions will allow more confident long-term predictions based on short duration laboratory studies. These complex evaluations are only now beginning.

The following sections include discussions of a simplified model of waste glass leaching, followed by a series of discussions of factors believed important to the leaching processes. In a few cases, e.g., effects of radiation and effects of thermal treatment, a large fraction of the total data available is summarized. In other cases, e.g., effect of pH, a small but representative fraction of available information is presented.

A. Leaching Model

The leaching behavior, or more specifically, the rate of mass loss of waste glass, can be generally described by a simple model, conceptually illustrated in Figure 2, adapted from Hughes et al. (1981). At very high flow rates, the glass "sees" an essentially infinite supply of water undersaturated in dissolution products and the mass loss is kinetically limited at a maximum rate determined by hydrolytic destruction of the glass network (leach rate limited). In the intermediate flow rate range, the contacting water is concentrated in silica leached from the glass matrix. The silica dissolution rate is then controlled by the rate at which the concentrated leachant is swept away and replaced by new solution. At the low end of the water flow rate scale, the rate of mass loss is determined by diffusion of dissolution products through essentially stagnant water or by the rate at which they are removed from solution by precipitation of minerals or formation of amorphous colloids. The leach rate limited and

Figure 2. Simplified behavior of glass in flowing water (adapted from Hughes, Marples and Stoneham 1981)

concentration limited portions of the model are supported in the following sections by flowing and static leach test data on 76-68 glass. Behavior in the low flow rate regime is very dependent on complex interactions between the waste package and the geology. This behavior is not yet well understood and will be addressed in the discussion section.

A.1 Flowing Tests: Relatively few studies using flowing leachants have been reported, particularly at slow flow rates. Figure 3 shows results from two flowing tests on 76-68 glass. Figures 3a and 3b illustrate that leach rates decrease with time to a steady state under flowing conditions. Figure 3b shows the wide range of elemental leach rates encountered in their series of tests using several leachants, three flow rates, and two temperatures. Figures 3c and 3d display the maximum, kinetically limited 76-68 glass degradation rate found at high water flow rates. Under these high flow conditions, the soluble and semi-soluble elements leach nearly congruently as seen by the convergence of the lines in Figure 3c.

As will be shown later, the very insoluble elements such as iron and zinc remain in the altered (gel) layer of the glass or are

Figure 3. a and b: Elemental releases from 76-68 glass in flowing tests as a function of time

c and d: Releases in flowing tests as a function of flow rate (a and c from Strachan and Exarhos 1981; b and d from Coles 1981)

reprecipitated on or within it. This low density, hydrated reaction layer also contains variable amounts of silicon and traces of more soluble elements. The maximum water-flow-rate insensitive mass loss is probably determined by transport through this gel layer or by the hydration reaction rate at the gel-glass interface (Shade and Clark, 1982). If transport limited, the rate could be determined by removal of dissolution products or by entry of attacking water species. In a later section, it is shown that the glass composition has large effects on this maximum mass loss rate.

A.2 Static Tests: Static data are helpful because they cover a broad range of conditions, and can provide understanding of kinetically limited mass loss, as well as the concentration limited losses. The parameters of interest in interpreting static tests are the ratio of sample surface area to solution volume (SA/V) and the product of this ratio by time ($t \cdot SA/V$).

Figures 4a and 4b from Pederson et al. (1982), illustrate static leaching behavior over a wide range of conditions. Figure 4a shows that, for tests run for 14 days, the amount released decreases with increasing SA/V. In the lower SA/V range (large water volumes) the leach rate is independent of water volume, being nearly flat as also seen in flow experiments at high flow rates (Figure 3c). Release plots for elements which are much more soluble than silicon, such as sodium and boron, curve downward with increasing SA/V because their release is controlled by the rate at which the silica glass matrix can be dissolved. Though not shown, highly insoluble elements such as iron, have very low normalized release at all SA/V values in Figure 4a. A group of elements with high-to-moderate solubility is seen to leach at essentially the same rate in the low SA/V region. At high SA/V, calcium release is limited by its moderate solubility, less than that of silicon.

Figure 4b demonstrates that the $t \cdot SA/V$ parameter uniquely defines the silicon release for tests performed with different volumes of water. A test performed at $SA/V = 1m^{-1}$ for 100 days produces the same silicon concentration in solution ($\sim 5 \times 10^{-4}$ moles/liter) as a test performed at $SA/V = 100m^{-1}$ for one day.

Figure 4. a. Elemental releases from 76-68 glass in static tests versus SA/V. b. Silicon releases as a function of time·SA/V (from Pederson et al. 1982)

Figures 5a and 5b (also from Pederson et al. 1982), further illustrate that the release rate of all elements is limited by the silicon dissolution rate. Figure 5a shows SIMS elemental depth profiles for samples leached 14 days at various SA/V ratios. In each case, the soluble elements, boron, sodium, and cesium, are depleted to the same depth as is silicon. They are more completely removed from the gel layer than silicon, which explains the somewhat higher sodium and boron releases compared to silicon at high SA/V in Figure 4a. This behavior is further addressed in the discussion section.

Figure 5b shows the direct effect of silicon solution concentration on glass leachability. In these tests, leachant compositions with various initial silicon concentrations were used to leach 76-68 glass for 28 days. In leachants where silicon concentration was initially high, the driving force for matrix dissolution was greatly reduced. In each case, the glass matrix was only dissolved enough to bring the silicon level in solution up to a maximum steady-state value near 120 ppm. As a result, boron release was found to be inversely related to initial silicon levels in solution.

Figure 6 from Strachan, 1982, shows depth profiles on 76-68 glass leached for one year at 90°C in deionized water at $SA/V = 10m^{-1}$. After this long time, the silicon had approached its concentration limit and leach rates had slowed to very low values. As the elemental profiles illustrate, even after one year, the depletion depth for all elements was the same as for silicon, about 55 microns (as compared to a maximum of about 8 microns in the 14-day profiles shown in Figure 5a). Iron and calcium are enriched in the gel layer, and zinc, cesium, and silicon are enriched near the surface, indicating the probable formation of alteration products there.

A.3. Solubility Data: As we have seen in the foregoing discussion, the concentration of silicon is an important, controlling parameter in leaching behavior. The specific solubilities of elements less soluble than silicon are also important in controlling their individual release rates.

Figure 5. a. Elemental depth profiles by SIMS on leached glass surfaces. b. Effect of silicon in solution on boron release (from Pederson et al. 1982)

Figure 6. Elemental depth profiles on 76-68 glass surface after one year of leaching (from Strachan 1982)

Silicon concentrations over amorphous silica have been determined as a function of temperature and pH by various investigators as shown in Figure 7. At 90°C, waste glass leachants (except for salt brines) tend to stabilize between pH 8 to 10.5. Although the silicon concentration in this pH range in Figure 7b is shown to be 200-300 ppm, most static leach tests at 90°C reach maximum silicon concentrations of 100-200 ppm. This is probably due to the presence of other glass dissolution products in the leachant.

Although there has been a significant increase in work toward understanding "solubility", data are still relatively limited for elements other than silicon. The question is of course far from simple

Figure 7. a. Effect of temperature on silicon solubility.
b. Effect of pH on silicon solubility at various temperatures (adapted from references shown on figures)

and will require evaluation of the effects of the waste package system, the influence of radiolysis, colloid formation, and effects of alteration products. Although a detailed discussion is outside the scope of this paper, important examples of the role of individual element solubility in leach performance are given in Figures 8 and 9. Figure 8, from Grambow (1982), shows results from a variety of tests on 76-68 glass plotted in terms of the ratio of normalized elemental mass losses of calcium to silicon versus pH of the solution. At low pH values where $NS_{Ca}/NL_{Si} = 1$, calcium concentrations are controlled by the rate of dissolution of silicon. At high pH values, the solid lines labeled Ca^{2+} and $CaCO_3$ are calculated (theoretical) values of solubility versus pH. It can be seen that the data are reasonably well explained (or at least limited by) solubility criteria. The use of EDTA as a complexant is shown to override the normal solubility restriction giving $NS_{Ca}/NL_{Si} = 1$ instead of ~ 0.01 . In Figure 9, data for Np, Am and Pu are plotted as concentration versus pH, taken from Rai and Strickert (1980). Concentrations achieved by contact with actinide-doped waste glass 76-68 were shown in this study to yield solubilities about the same as for the pure oxides. This is favorable since solubilities of the transuranium oxides are very low under expected repository conditions. Comparable studies in salt brines where complex formation can be a factor will be important.

A.4 Application of Laboratory Data to the Leaching Model: In this section, the static and flowing test data are combined and related to the conceptualized model shown in Figure 2.

The results of static leach tests can be related to those performed under flowing conditions by adopting the concept that leaching a glass sample statically in a large container of water for a specified time is equivalent to leaching it in a smaller container through which the same total volume of water passes in the same specified time. A static test in 100 ml of water for 100 days is therefore equivalent to

Figure 8. Ratio of calcium release versus silicon release as a function of pH in static leaching studies (from Grambow 1982)

a flowing test lasting 100 days at a flow rate of 1 ml per day, assuming a comparatively small dead volume is present. While this assumption has some obvious limitations, comparison of the available static and flowing data on 76-68 glass shows that the problems are of secondary magnitude, relative to the general trends reflected over the wide range of test conditions considered.

The data are combined in Figure 10 through the use of a flow parameter with units of meters per day. For the flowing data, this parameter is calculated by dividing the water flow rate, $Q(\text{m}^3/\text{d})$, by the sample surface area, $SA(\text{m}^2)$. For the static data, division of the water volume, $V(\text{m}^3)$ by the product of the sample surface area and the leaching time (t) yields the flow parameter. Composition normalized

Figure 9. Solubilities of Np, Pu, and Am as a function of pH (adapted from Rai and Strickert 1980)

Figure 10. Elemental Release Rates as a Function of Flow Parameter for 76-68 Glass

elemental release rates are plotted in Figure 10 so that sodium release can be compared to silicon release. The line for silicon concentration control was applied to the figure by normalizing to the weight fraction of silicon in 76-68 glass. This line represents what the silicon release rate would be if it were always controlled by maximum silicon concentration in solution at 200 ppm.

The concept utilized to obtain Figure 10 can be described algebraically as follows. Consider first, a continuous flow experiment. At steady state, the effluent concentration (C_{ss}) is directly related to the leach rate (R_f):

$$R_f = \frac{C_{ss} \cdot Q}{SA} = C_{ss} \cdot F_f, \text{ where } F_f = \frac{Q}{SA}.$$

At very low flow rates $C_{ss} \approx C_s$, where C_s is the solubility limit.

For static tests, the apparent leach rate is:

$$R_s = \frac{C_t \cdot V}{SA \cdot \Delta t} = C_t \cdot F_s, \text{ where } F_s = \frac{V}{SA \cdot \Delta t}, \text{ and } C_t \text{ is the}$$

concentration at time t . At long times in a static experiment, $C_t = C_s$. Under conditions of low flow rate (flow experiment) or long times (static experiment) it is clear that:

$$R_f = C_s \cdot F_f \text{ and } R_s = C_s \cdot F_s.$$

Hence,

$$\frac{R_f}{F_f} = \frac{R_s}{F_s} = C_s.$$

This equality is thus the basis for adjusting static and flow leach rates using the flow parameters F_f and F_s . It should be noted that

the correlation is less justified for high flow rate/short time comparisons. Considering the assumptions the agreement is nevertheless quite good for all conditions plotted in Figure 10.

The silicon data in Figure 10 display the leach-rate limited and concentration-limited behaviors shown conceptually in Figure 2. In none of the tests was the silicon release rate higher than that predicted by the 200 ppm concentration limit. Good agreement is seen between the 90°C flowing and static data (closed and open circles) and between the 70°C quasi-flowing and static data (closed and open inverted triangles). Coles' 75°C flowing data (closed squares) indicate a kinetically limited leach rate about four times slower than that from the 90°C data of Strachan and Exarhos (closed circles). The differences among all of the silicon data are surprisingly small considering the tests were performed from 0.4 to 420 days on different samples of 76-68 glass at three different laboratories using five different techniques.

In the discussion section, consideration is given to the sodium data (open triangles) in Figure 10 and the lack of the minimum leach rate "tail" shown conceptually in Figure 2 at low flow rates.

B. Factors Modifying Leaching Behavior

In this section, we discuss factors which affect leaching behavior and how they can be expected to modify the model presented in the previous section. The primary variables include temperature, pH, the leachant composition, the glass composition, thermal history, and radiation effects.

B.1 Effect of Temperature: The single most important variable in the leaching process is temperature. The poor performance of glass at relatively high temperatures (>200°C) in large part led to major

development efforts on crystalline waste forms such as Synroc. Of course it is not obvious that water need be allowed to contact the waste package let alone the glass block during the early storage period when temperatures are high. It nevertheless is desirable to develop glasses which are relatively insensitive to temperature. The temperature dependence has therefore been evaluated for a number of compositions. Figure 11 summarizes a major fraction of the information available, obtained over the temperature range 25 - 300°C under a variety of experimental conditions. It should be pointed out that the data in Figure 11 have all been normalized to an arbitrary leach rate ($\log R=0$) at 50°C. "Average" leach rate increases in dilute conditions and the temperatures at which those increases would be observed are as follows: (x1)50°C, (x10)95°C, (x100)150°C, (x1000)220°C.

A few points about Figure 11 are worth noting as follows: low temperature data generally result in very low leachate concentrations compared to high temperature data. Hence numerous studies show an apparent leach rate suppression at high temperatures which we interpret as often due to silicon concentration limitations. In tests where $\text{time} \cdot \text{SA/V}$ is large enough to saturate silicon, the temperature dependence of silicon solubility (Figure 7a) will directly control the apparent temperature dependence of the leach rate. Differences between elements and for different groundwaters may be significant. For example, in Figure 11 compare line 1 (Mo) to line 2 (Si). The data shown are from solution analysis (lines 1-3 and 9-12), or by weight loss (lines 4-7). There are no detailed studies which include measurement of reaction depth as a function of temperature. Activation energies obtained from the slopes of bounding lines in Figure 11 range from 17-35 Kcal/mole. Very recent studies by Shade and Clark (1982), for glass 76-68, at high solution dilutions, gave an element independent activation energy of 8 ± 2 Kcal/mole for the forward reaction. Based on discussions in the preceding section and as interpreted independently by Shade and Clark, this activation energy is

Figure 11. Temperature dependence for leaching of various waste glasses. Leach rate is in arbitrary units, normalized to leach rate = 1 at 50°C. References as follows:
 1,2/Westsik et al. (1980); 3/Reeve et al. (1981);
 4-7/Boult et al. (1979); 8/Westsik and Peters (1981);
 9-12/Chick and Buckwalter (1980).

believed to be directly related to hydrolytic reactions of the silica matrix.

B.2 Effect of pH: The pH sensitivity for waste glass leaching is an obvious performance variable, interrelated to all of the other parameters since the pH changes as alkali leaches from the glass. It is our interpretation that (with the most probable conditions) in a

hard rock repository (low groundwater flow rate) the pH at the surface of the glass undergoing leaching will be controlled by the glass/radiation field rather than by the pH of the groundwater. In concentrated salt brine, the evidence is that the salt brine and the radiation field will be controlling. This still leaves a wide range of possible pH values depending on flow rate, the radiation field, and the durability of the glass. The pH, in essence, will be controlled by competition between leached alkali--driving the pH basic to 9 or 10; and gamma and alpha radiolysis--driving the pH acid to as low as 3 (McVay and Pederson 1981).

Figures 12a and 12b show the effect of pH on leach rate for several waste glass compositions. The remarkable difference between nuclear waste glasses and commercial compositions (e.g., container glass - Fig. 12c) can be explained by the relatively high concentration of transition and rare earth oxides in waste glass compositions. Under most leaching conditions these oxides are insoluble, and dramatically improve corrosion resistance at high pH. At low pH they become soluble and do not have a protective influence. At the same time, the bottle glass network, which contains more silica than does waste glass, exhibits excellent acid durability but poor caustic resistance, exactly paralleling the solubility of pure SiO_2 .

B.3 Effect of Leachant Composition: As in the previous areas, it is difficult to consider groundwater effects without at the same time considering other factors, particularly pH and radiolysis effects. In the case of hard-rock repositories, groundwater silica concentrations will directly affect release rates as shown in Figure 5b, earlier. There will also be significant differences between leaching in salt brines (neutral or slightly acid pH) compared to moderate ionic strength hard rock groundwater with basic pH. From the data now available, differences nevertheless appear to be relatively small. Figure 13 shows Pu and Si results for glass 76-68, obtained by the IAEA method with periodic water exchanges, therefore simulating flowing conditions. The spread in leach rates is only about one order

Figure 12. Effect of pH on glass leach rates (adapted from Mendel et al., 1981, and references therein)

Figure 13. Effect of synthetic groundwaters on leachability (adapted from Bradley et al. 1979)

Figure 14. Long duration static leach test results for glass 76-68 comparing deionized water to salt brine behavior (adapted from Strachan 1982)

of magnitude for the five generic solutions studied. Figure 14 shows silicon leach rates and penetration depths for glass 76-68 using the static MCC-1 leach test, comparing deionized water to brine. Remarkably, leach depths after one year are approximately the same, even though the pH was 9.5 in H_2O compared to 6.5 in brine. In water, the leaching process has slowed markedly at long times, which is interpreted as due to silica reaching its solution concentration limit. In brine, the silicon concentration in the solution begins to decrease after about 100 days. Strachan (1982) interprets this as due to the formation of an alteration product, probably sepiolite which removes the silicon from solution at a faster rate than it is being released from the glass. This results in the increasing leach depth at one year for brine as opposed to the constant leach depth for water. The effects of alteration product formation on repository leaching are addressed further in the discussion section. (Solid state concentration profiles from this study were discussed earlier, Figure 6).

Figure 15 compares behavior (MCC-1) in tuff, basalt and deionized water for soluble elements in 76-68 glass. The leach rate depressions in tuff and basalt are due to silica concentrations already present in the groundwater. The more important information present in this figure is the shaded band, representing leachate concentrations under the same conditions except that a coupon of iron was added to the leach vessel ($SA_{iron}/SA_{glass} = 1$). In that case there is essentially no groundwater effect on leach performance and leach rates are enhanced even compared to deionized water. This unexpected result arises from formation of colloidal (and precipitated) iron silicate such that the usual retardation effects related to silica approaching its concentration limit are not operative. Obviously, more work is needed to define performance of waste glass under conditions closely simulating waste package designs. Previous work by Buckwalter and Pederson (1981), showed that the presence of metallic lead could reduce glass leach rates by at least several orders of magnitude, though such controls have not been considered in waste package designs.

Figure 15. Effect of groundwaters and metallic iron on releases from glass 76-68 (from Pederson et al. 1982)

B.4 Effect of Glass Composition: Flowing leach tests have not been performed on a variety of glass compositions, however, enough static test data is available to infer the effects of composition on our leaching model. Figure 16a shows the silicon release up to 28 days at 90°C and $\text{SA/V} = 10\text{m}^{-1}$ for 76-68 glass and several lower leach rate borosilicate waste glasses. The best of these released about 1/30 as much silicon in 28 days as did 76-68 glass. Release of other elements was controlled by silicon matrix dissolution, as expected. If Figure 10 were reproduced for these lower leach rate glasses, only the high flow rate data would be affected. There would be an order of magnitude reduction in the maximum rate of mass loss (leach rate limited) in the high flow parameter regime. Mass loss would be independent of water flow rate down to lower flow parameter values. At lower water flow rates, where silicon concentration controls, these glasses would be expected to behave similarly to 76-68 glass, i.e., the advantage afforded by improved glass compositions is greatest at high water flow rates.

Figure 16. a. Silicon release as a function of time from 76-68 and lower leach rate glasses. b. Range of silicon release as a function of temperature for glasses in Figure 16a (adapted from Chick and Buckwalter 1980)

Figure 16b shows the effect of temperature on leaching of the glasses from Figure 16a. Silicon releases become nearly identical for all these glasses at 200°C. Thus the advantage of improved glass compositions appears greatest at the lower temperatures. However, since silicon concentrations at the higher temperatures were nearing 300 ppm in these tests, silicon concentration effects may be masking a continued high-temperature advantage for the improved glasses.

B.5 Effect of Thermal History: As a metastable disordered solid, glasses tend toward the crystalline state at all temperatures significantly below the liquidus temperature. Crystallization kinetics have been measured for some waste glass compositions, and so-called time-temperature-transformation curves can be constructed as in Figure 17. These curves define the time-temperature combinations which produce 5 wt% ingrowth of crystals under anhydrous conditions. Areas outside the curves define the vitreous state. Work by Doremus (1973) shows a strong influence of water vapor on crystallization rates not considered further here. We assume the glass will be sealed in metal canisters until temperatures are low relative to the crystal formation range.

Depending on cooling history from the melting temperature, and depending on the glass, some crystallization can also occur at the time of preparation, hence leach performance of partially crystallized glasses has been evaluated in both the U.S.A. and Europe. Figure 18 shows leach rates of a variety of glasses measured after annealing for two months at the temperatures indicated. In the worst case, the leach rate increase for the borosilicate glasses is one order of magnitude. Several of the European glasses show no increase in leach rate (or in fact improve) as a result of crystallization. Phosphate glasses, as known from previous work, are more sensitive to devitrification. Two points about Figure 18 are important. First, the crystal yields for

Figure 17. Time-temperature-transformation (TTT) curves for glasses PNL 72-68, 76-68 and 77-260 (adapted from Turcotte et al. 1980)

Figure 18. Effect of crystallization on leach rate (two-month heat treatment at the temperatures indicated) (solid curves adapted from Westsik 1979; dashed curves adapted from Malow et al. 1980)

most of the glasses after two months is in the range 30-50% at $\sim 700^{\circ}\text{C}$; hence, this is a severe test. After pouring into the canister, even the centerline of the waste glass cylinder will cool to below 500°C within five days. Secondly, the temperature at which the maximum crystallinity occurs is quite glass insensitive because the glasses all have similar viscosities; hence, similar crystallization kinetics (Figure 17).

It is interesting to note that two leach rate axes (differing by four orders of magnitude) are required to present the data in Figure 18. Although all of the data were obtained by the Soxhlet method, Malow et al. (1980) used monolithic plates whereas crushed glass was used in the U.S.A. work (Westsik, 1979). Thus, the effective SA/V ratio was much higher in the tests with crushed glass, leading to a significant depression in the apparent leach rate, as discussed previously and shown in Figures 4a and 4b.

B.6 Effect of Radiation: Other than the extraordinary mixture of elements (~ 30) contained in nuclear waste glass, its most important distinguishing characteristic is its self-radioactivity. With respect to leaching, there are two fundamental questions: "Do the properties of the solid change?" and "Are there solution chemistry-radiolytic processes of importance?" With regard to solution chemistry effects, the primary effect is to drive leachant pH acid (McVay and Pederson, 1981; Rai, Strickert and Ryan, 1980). Gamma radiation, potentially important only for about the first 300 years after emplacement, causes acid pH when oxygen is present in the water. Without oxygen, gamma radiation causes formation of free radicals whose effect on, for instance, actinide solubilities is presently unknown. Alpha decay is potentially more of a problem because it will continue for thousands of years after emplacement. Alpha radiolysis causes acid pH even without oxygen present, as long as dissolved nitrogen is contained in the water. In the presence of nitrogen, alpha decay produces conditions slightly more oxidizing than those in air-saturated water. This will tend to increase the solubility of actinides over their solubilities in reducing conditions. However, most laboratory measurements of

actinide solubilities have been performed under oxidizing conditions. Solubilities shown earlier in Figure 9, for instance, are derived from work by Rai and Strickert using a quinhydrone buffer which maintains oxidizing conditions.

The question of solid state changes has two parts, the first related to short-lived fission products and the high ionizing radiation field created during the first few hundred years and the second at long times, related to the decay of actinides. Actinide decay causes atomic displacements (up to ~ 1 dpa) and also contributes high doses of ionizing radiation through slowing down of the 5 MeV α particles. During the first few hundred years there are also considerable chemical changes introduced through transmutation (e.g., Cs $\rightarrow$ Ba), but these are not likely important, given the complexity of waste glass compositions. Work by Gray (1982) suggests that transmutation effects on leach rates are small.

With regard to changes in leach rate arising from ionizing radiation damage to the glass, there is actually very little definitive data at the high doses that will be reached in commercial waste glasses. Figure 19a summarizes our current understanding of property changes. The leach rate measurements come from limited electron bombardment studies and suggest the radiation-induced changes are relatively small even though there may be significant volumetric changes. This probability of only small effects from ionizing damage is supported by much stronger evidence obtained from studies of actinide decay where both high displacement damage and high ionization damage occur. Figures 19b and c show that although alpha decay can cause swelling or densification up to $\sim 1\%$, the effect on leach rate is negligible. It should be noted that the low apparent leach rates for Glasses 4, 5 and 6 arise from calculating leach rates based on Cm versus weight loss (all others).

Figure 19. a. Summary of ionizing radiation effects (from Weber and Turcotte, 1982). b. Effect of actinide decay on density (solid curves from Roberts et al., 1981; dashed curves from Malow et al., 1980). c. Leaching comparison of unirradiated and fully radiation-damaged glasses (adapted from Turcotte, 1982).

IV. DISCUSSION

In this section, we discuss the most important uncertainties involved in using the existing laboratory leaching data to estimate glass performance in a repository. Considering the material presented in Section III, calculation of elemental release rates from glass in a repository requires that important assumptions must be made in the following areas:

- A) repository leaching temperature,
- B) repository leaching pH,
- C) repository flow parameter,
- D) control of soluble element release by silicon, and
- E) alteration product formation rates.

Enough information exists to make reasonably conservative assumptions in the first four areas as discussed below. Alteration product formation and its effects on glass release in the repository remains the largest uncertainty.

A. Repository Leaching Temperature

Estimates of commercial high level waste repository temperatures for four geologies are presented in a series of recent draft documents by the Reference Repository Conditions Interface Working Group (RRCIWG, 1982). Effects of some design parameters and independent variables on temperature are illustrated in Figure 20. The curves show that maximum centerline temperatures are reached at less than ten years for commercial HLW. Various assumptions were made in calculating the temperature curves, depending upon the particular repository geology in question. Temperatures for basalt, granite, and salt were calculated assuming a dry repository. Since the inflow of water would increase thermal conductivities and lower temperatures, the curves for these geologies are conservative for predicting leaching temperatures. The effect of heat loading is illustrated by comparison of curves 2 and 3. Curve 3

Figure 20. Estimated canister centerline temperatures versus time after emplacement (adapted from RRCIWG draft reports, 1982)

is for lower heat defense waste and peaks 105°C lower than does curve 2. The amount of waste stored per unit volume in the repository is a design parameter which can control the maximum temperature by controlling the heat loading. Curves 2 and 6 for granite and salt with commercial waste at 25 watts/m² illustrate the effect of geology choice on temperature. Curves 4 and 5 illustrate the influence of liquid water on the thermal characteristics of the repository. For curve 4, it is assumed that the pressure is high enough to keep water in the condensed state. The resulting maximum temperature is 50°C less than on curve 5 for which it was assumed that pressure was low enough to allow water over 100°C to vaporize.

If water were to enter the repository soon after emplacement, canister centerline temperatures should cool to below 100°C by 100 years (as for curve 4). It is therefore reasonable to assume that the waste package can be designed to assure that water does not contact the glass before cooling to below 100°C. Other options for reducing maximum possible leaching temperatures include reducing the waste loading or the canister packing densities assumed in the RRCIWG documents, or using interim storage to allow the canisters to further cool before emplacement in the repository.

B. Repository Leaching pH

The NWTS documents list equilibrium groundwater pH's in the range from 6 to 9 depending upon geology and temperature. At low flow rates, glass dissolution and radioactivity could have a large influence on the pH of water near the glass surface. Under static or low-flow conditions, glass dissolution products tend to raise the pH. On the other hand, radiolysis of water tends to produce acid pH's. The effective pH attained at steady state under low flow conditions will depend upon the relative magnitude of glass dissolution, radiolysis, and interactions with the geology. If the pH near the glass surface remains between about 4 and 10, then release rates due to matrix dissolution can be

expected to be equal to or less than those experienced under laboratory static leaching conditions which yield steady-state pH values of 8 to 10.5 at 90°C. At 90°C and below, it is considered unlikely that pH could rise above 10. However, an increased understanding of the effects of radiolysis will be necessary in order to estimate the likelihood of pH falling below 4. If the pH near the glass were to reach very low values due to radiolysis, higher elemental releases could result as seen in Figure 12b. But, as the leachant was carried away from the waste package, the pH would soon return to values moderated by the geology (pH 6 - 9). Elements less soluble at pH 9 than at pH 3 such as americium, would then precipitate out of solution. However, soluble elements such as cesium may remain dissolved. Until pertinent waste package leach testing is performed using radioactive materials and a variety of conditions, predictions of effective leaching pH will be somewhat uncertain.

C. Repository Flow Parameter

Some information is available about repository groundwater flow rates under both normal and accident conditions. Mass transfer calculations must be applied to accurately estimate the removal rates of dissolution products by slowly flowing groundwaters. However, some simplistic assumptions can be applied to show that under normal circumstances, hard-rock repository leaching should occur at effective flow parameters well into the silicon concentration-controlled regime in Figure 10.

A range of normal groundwater flow velocities for a basalt repository of 0.1 to 0.2 meters per year was published by Dove et al. (1982). These water velocities assumed a rock porosity of 0.06 so the equivalent range of Darcy velocities is 2 to 4×10^{-5} m/d. These rates do not take into account the benefit of a backfill barrier and are

considered by the authors to be conservatively high. Smith et al. (1980) estimated basalt repository flow rates equivalent to values one to three orders of magnitude slower than these. Lacking similar data for other geologies, Dove's values are assumed to be reasonably conservative estimates for velocities in granite or tuff as well as basalt. No significant groundwater flow is expected to occur in salt repositories except under abnormal conditions. Dove et al. (1982) also estimated flow rates through waste packages in basalt for an accident scenario in which a water-filled fault intersects the waste package. The probability of such an accident occurring has been estimated (A.D. Little, Inc., 1980) to be 5×10^{-7} per year or smaller. It would also affect only a few of the total number of canisters. Water flow rates in the fault were estimated to range between 0.1 to $1.0 \text{ m}^3/\text{year}$ per meter width of fault. The authors estimated the maximum flow that can pass through a waste package is that flowing in the fault plane across a width equal to twice the waste package emplacement hole diameter. Hole diameters for a repository in basalt were assumed in NWTs-16 to be 0.5 meters. Based on these assumptions, the water flow through the waste package remnant would range from 0.1 to $1.0 \text{ m}^3/\text{year}$ in the case of the fault scenario.

In order to relate our laboratory-based leaching data to the repository flow rates, it is necessary to make some assumptions about the configuration and surface area of glass in the waste package. The canister is assumed to be ten feet (3.1m) tall and one foot (0.31m) in diameter, with a geometric surface area of 3.1 m^2 . The glass is expected to crack while the canister cools after filling, such that the total surface area of glass is up to twenty times the geometric surface area of the cylinder. However, under normal circumstances, many of these cracks are expected to remain tightly closed, not permitting water flow and leaching (Westsik and Perez, 1981). Therefore, it is reasonable to assume that the surface area of glass available for leaching will be from one to ten times the geometric cylinder surface area, or from 3.1 to 31 m^2 .

Calculation of a repository relevant flow parameter (m/d) as used in Figure 10 from the Darcy flow velocity and the glass surface area is not simple as in the case of the laboratory tests. The problem is that, while laboratory leaching specimens are contained in vessels with well-defined boundaries, a canister of glass in a repository is immersed in an effectively infinite flow field. Mass transfer (diffusion/convection) calculations such as those utilized by Chambre' et al. (1982) should be utilized to estimate the removal rates of dissolution products in a repository. A more simplistic approach (which is not entirely valid) is to assume that the canister of glass is effectively surrounded by a container and that the water flowing through this imaginary container is essentially homogeneous. The results from such a "stirred tank" assumption depend heavily upon the choice of the tank size. Choosing an effective glass surface area of 31 m^2 , a "stirred tank" the same size as the canister, and a Darcy velocity of $4 \times 10^{-5} \text{ m/d}$, the resulting flow parameter would be $1.3 \times 10^{-6} \text{ m/d}$. Referring to Figure 10, this flow parameter is well down the curve in the silicon concentration controlled regime of leaching behavior. Assuming a faulted repository scenario, the volumetric water flow rate could be as high as $1 \text{ m}^3/\text{d}$ as discussed previously. The resulting flow parameter for 31 m^2 of glass surface area would be about $1 \times 10^{-4} \text{ m/d}$. This is still within the silicon concentration controlled regime on Figure 10. One can conclude from these rather simplistic calculations that effective flow parameters in normal (unfaulted) hard-rock repository operation should be well down in the silicon concentration controlled regime. Actual estimation of a reasonable flow parameter for normal repository leaching and the calculation of expected release rates is left to other authors including Schneider et al. (1982) in the companion document to this report.

D. Control of Soluble Element Release by Silicon

We have claimed previously that release rates of soluble elements such as sodium and boron are controlled by the release rate of silicon. Yet, as seen in Figure 4a, although releases of the more soluble elements decrease with that of silicon, they remain somewhat higher. The sodium release rates from Pederson et al. (1982) shown in Figure 10 are a factor of about 1.5 greater than those for silicon at high equivalent flow rates and up to a factor of 10 greater at the lowest flow parameter tested. As discussed in the following paragraph, the soluble elements cannot be released from the glass until the silica is hydrated. This is concluded based on the observation that the depletion depths of the soluble elements are never deeper than that of silicon. The normalized release differences are due to variations in the extent to which elements are depleted from the gel layer.

As seen in the elemental depth profiles in Figure 5a, although the soluble elements are never depleted to any greater depth than is silicon, they are more effectively depleted from the gel layer than is silicon. In the thick gel layer ($\sim 8 \mu\text{m}$) on the sample from the $\text{SA/V} = 1 \text{ m}^{-1}$ experiment, silicon is depleted by nearly a factor of 10 and sodium is depleted by a factor of about 100. This means that 90% of the silicon from the gel layer is in solution as is 99% of the sodium. Their composition normalized releases, based on solution concentration should be fairly close under these conditions. In the very thin gel layer ($\sim 0.3 \mu\text{m}$) produced by the experiment at $\text{SA/V} = 1.6 \times 10^4 \text{ m}^{-1}$, 90% of the sodium but only 20% of the silicon from the gel layer have been released into solution. Thus, the discrepancy between composition normalized silicon and sodium releases increases with increasing SA/V. This explains the Pederson et al. data in Figure 10.

It is clear then, that the silicon hydrolysis rate controls release of the more soluble elements, but that the extent of that control depends upon the specific leaching conditions. For estimating release rates of very soluble radionuclides from glass in a repository, it would be prudent to rely more on sodium data than on silicon data.

E. Alteration Product Formation Rates

The largest uncertainty in estimation of glass release rates in a repository has to do with the position of the low flow rate "tail" of the conceptualized mass loss curve in Figure 2. As mentioned earlier, this portion of the curve represents an expected minimum, flow-velocity-independent rate of mass loss. This minimum leach rate is established either by the rate at which dissolved silicon is diffused away from the glass or by the rate at which it is precipitated into alteration products. Either mechanism will, by removing dissolved silicon from the solution, allow more silicon to be released by the glass. No minimum leach rate tail is evident in the low flow data shown in Figure 10. Diffusion could not effect these results because they were obtained in closed containers, not the open flow field of a repository. Because of their limited duration and lack of the presence of repository minerals, these tests did not produce alteration products in significant enough quantities to remove silicon from solution. As discussed in the section on the effects of leachant composition, Strachan's (1982) data on one-year static leaching in brine showed that alteration products including sepiolite $[\text{Mg}_2\text{Si}_3\text{O}_7(\text{OH})_4]$ were forming after about 100 days at a rate fast enough to decrease the silicon concentration in solution (Figure 14). This resulted in a greater altered layer depth after one year in brine than in water, even though both the pH and the silicon solubility are lower in the brine.

At issue is where the low flow rate "tail" would intersect the silicon concentration controlled portion of the curve in Figure 10 if the tests were performed in a repository environment. Since Strachan's test was conducted at $\text{SA}/\text{V} = 10 \text{ m}^{-1}$, at 100 days, the flow parameter, $\text{V}/(\text{SA} \cdot \text{time})$, was 10^{-3} m/d . This indicates that, in salt brine, the tail might intersect in Figure 10 at the high end of the silicon-controlled regime. Long duration SA/V experiments in brine are needed to verify this.

It should be reiterated that regardless of the alteration product formation rates, silicon (and therefore the most soluble radionuclides) cannot be released from the glass faster (at 90°C) than the kinetically-controlled rate in the high flow parameter regime in Figure 10. Recall also that at 90°C, improved glasses have kinetically controlled release rates from ten to thirty times slower than that for 76-68 glass at a flow parameter of 3.6×10^{-3} m/d (see Figure 16a). This indicates (Figure 10) that, regardless of any unfavorable alteration product formation, normalized release rates of even the most soluble radionuclides are likely to be less than 10^{-1} g/m²·d for improved glass formulations.

One type of alteration product which could present a two-fold problem are colloids. Colloids can provide a silicon sink (as discussed in Section B.3), removing silicon from the saturated solution near the glass and resulting in accelerated matrix dissolution up to the kinetically limited rate. Additionally, depending upon the solution pH, some actinides can be adsorbed by the colloids. The probability of actinide-containing colloids being transported through the porous rock and away from the repository is unknown, but is an important area under current investigation.

V. CONCLUSIONS

Static and flowing laboratory leaching data support a model which predicts that:

- At high water flow rates the rate of mass loss from the glass is kinetically limited to a maximum value.
- At intermediate flow rates, silicon concentration in solution controls the rate of mass loss.

- At lower flow rates or under static conditions, the rate of mass loss from the glass is determined by the diffusion of silicon through the water or by alteration product formation rates.

Evaluation of the effects of various parameters on leaching behavior has shown that:

- Temperature is important; the kinetically-limited rate of mass loss approximately doubles with each 10⁰C increase.
- The pH has small effects within the 4-10 range.
- The effect of leachant chemical composition is most important with regard to its influence on alteration product formation.
- Glass composition exhibits the largest effects at high flow rates where improved glasses leach from ten to thirty times slower than 76-68 glass.
- The effects of the thermal history (devitrification) of the glass are not likely to be significant.
- Radiation effects are important mainly in that radiolysis can potentially cause leachant pH values less than 4. Radiation damage of the glass causes insignificant changes in leach performance.

In order to use the existing laboratory leaching data to estimate elemental releases from glass under repository conditions, the most important assumptions concern five areas. In the first four areas, enough knowledge probably exists to make reasonably conservative assumptions. In the last area, more information is needed:

- In this report we have assumed that water can be kept from contacting the glass until repository temperatures are below 100⁰C.

- If the pH of the repository water remains between about 4 and 10, leach rates will not be significantly increased. More data is needed to determine if radiolysis will drive the pH to less than 4 where leach rates are predictable, but potentially high.
- The effective repository water flow rates in hard-rock geologies should be rigorously calculated. However, they will probably be low enough that glass leach rates will be controlled by silicon concentrations in solution or by diffusion in the leachant or alteration product formation rates.
- In the silicon concentration limited regime, release rates of more soluble elements can still be up to a factor of ten higher than that of silicon. Thus, sodium release rates should be used to estimate soluble radionuclide releases from glass in a repository.
- Alteration product formation rates and colloid formation and transport probably present the largest uncertainties in predicting glass release under repository conditions. Although more information is needed in this area, radionuclides can nevertheless be released no faster than the kinetically limited leach rate of the glass.

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FIGURE CAPTIONS

- Figure 1a. Ternary diagram of glass formers, modifiers and intermediates, showing nuclear waste glass composition experimental region (from Chick et al. 1981)
- Figure 1b. Composition region for waste glass development study in Japan (from K. Ishiguro, Power Reactor and Nuclear Fuel Development Corporation, Japan)
- Figure 2. Simplified behavior of glass in flowing water (adapted from Hughes, Marples and Stoneham 1981)
- Figure 3. a and b: Elemental releases from 76-68 glass in flowing tests as a function of time
c and d: Releases in flowing tests as a function of flow rate (a and c from Strachan and Exarhos 1981; b and c from Coles 1981)
- Figure 4. a. Elemental releases from 76-68 glass in static tests versus SA/V. b. Silicon releases as a function of time•SA/V (from Pederson et al. 1982)
- Figure 5. a. Elemental depth profiles by SIMS on leached glass surfaces. b. Effect of silicon in solution on boron release (from Pederson et al. 1982)
- Figure 6. Elemental depth profiles on 76-68 glass surface after one year of leaching (from Strachan 1982)
- Figure 7. a. Effect of temperature on silicon solubility. b. Effect of pH on silicon solubility at various temperatures (adapted from references shown on figures)
- Figure 8. Ratio of calcium release versus silicon release as a function of pH in static leaching studies (from Grambow 1982)
- Figure 9. Solubilities of Np, Pu, and Am as a function of pH (adapted from Rai and Strickert 1980)
- Figure 10. Elemental release rates as a function of flow parameter for 76-68 glass (references shown in figure)
- Figure 11. Temperature dependence for leaching of various waste glasses. Leach rate is in arbitrary units, normalized to leach rate = 1 at 50°C. References as follows: 1,2/Westsik et al. (1980); 3/Reeve et al. (1981); 4-7/Boult et al. (1979); 8/Westsik and Peters (1981); 9-12/Chick and Buckwalter (1980).

- Figure 12. Effect of pH on glass leach rates (adapted from Mendel, et al. 1981 and references therein)
- Figure 13. Effect of synthetic groundwaters on leachability (adapted from Bradley et al. 1979)
- Figure 14. Long duration static leach test results for glass 76-68 comparing deionized water to salt brine behavior (adapted from Strachan 1982)
- Figure 15. Effect of groundwaters and metallic iron on releases from glass 76-68 (from Pederson et al. 1982)
- Figure 16. a. Silicon release as a function of time from 76-68 and lower leach rate glasses. b. Range of silicon release as a function of temperature for glasses in Figure 16a (adapted from Chick and Buckwalter 1980)
- Figure 17. Time-temperature-transformation (TTT) curves for glasses PNL 72-68, 76-68 and 77-260 (adapted from Turcotte et al. 1980)
- Figure 18. Effect of crystallization on leach rate (two-month heat treatment at the temperatures indicated) (solid curves adapted from Westsik 1979, dashed curves adapted from Malow et al. 1980)
- Figure 19. a. Summary of ionizing radiation effects (from Weber and Turcotte 1982). b. Effect of actinide decay on density (solid curves from Roberts et al. 1981, dashed curves from Malow et al. 1980). c. Leaching comparison of unirradiated and fully radiation-damaged glasses (adapted from Turcotte, 1982).
- Figure 20. Estimated canister centerline temperatures versus time after emplacement (adapted from RRCIWG draft reports 1982)

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