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Elemental Release from Glass and Spent Fuel

Technical Report

October, 1981

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There are fundamental differences in the interactions of simple silicate and complex borosilicate waste glasses with aqueous solutions. Therefore, predictive models and/or results derived from simple silicate glasses cannot, in general, be used to predict the behavior of complex borosilicate glasses. Additionally, it has been shown that realistic flow rates and ground-water differences do not alter elemental release from glass or spent fuel by amounts greater than one order of magnitude.

The solubility limits for actinides contained in glasses have been shown to be identical to those observed for crystalline actinide oxide states themselves. Therefore, thermodynamic arguments can be used to predict the upper limits of actinide isotopes in solution.

Radiolysis effects in the absence of air have been shown to be important at lower temperatures but not significant at elevated temperatures expected in a repository. However, if air (perhaps just nitrogen) is present, nitric acid is generated as a radiolysis product which greatly enhances elemental removal at all temperatures.

Spent fuel leaching is less sensitive to temperature change than glass and, in some cases, shows a negative temperature dependence. As the oxygen content of the leachate decreases, actinide removal also decreases from both glass and spent fuel.

In general, existing release models for glass and spent fuel are not adequate to predict long-term behavior in a meaningful and believable manner. However, enough understanding has been and is being generated that the next version of predictive equations should be capable of defensible predictions based on mechanistic understanding.

The results of these preliminary studies are discussed in this report. More detailed testing with site-specific ground waters and package components under expected repository conditions are under way and will be the subject of future reports.

water flow. In such a situation the nuclear waste is not expected to pose a threat to the health and safety of the public. It is generally agreed that the principal mechanism by which waste isolated in this manner could reach the biosphere is if the waste is contacted by ground water which will leach some radionuclides and subsequently transport them to the biosphere. For a number of years, therefore, research efforts have been in progress to determine how, and at what rate, radionuclides are released from various potential waste forms when contacted by ground waters. The results of that research are the subject of this report.

In the concept of deep geologic isolation, the waste form will be a solid. A wide variety of possible waste forms have been suggested and many of these have been investigated to some extent, mainly ceramics and glasses. Over the years glass has continued to be a primary candidate waste form because of its physical stability, chemical inertness, ability to accommodate a wide variety of radioisotopes, and ease of fabrication. In the U.S., the possible disposal of spent fuel is also being considered. In this report we will concentrate the discussion on the two types of materials on which the most research has been done, glass and spent fuel.

The waste form is only one part of a waste package system which may eventually be emplaced in a deep geologic repository. This is illustrated in Figure 1-1. The package as presently conceived is a multibarrier system consisting of the waste form, its container and possibly an overpack to the container, and/or a sleeve. The final barrier might be backfill placed between the host rock and the other package components. The reactions of each of these components with ground waters are important to the overall performance of the package, and research on their interactions is presently under way. These interactions will not be discussed in this report except as they directly influence leaching of the waste form.

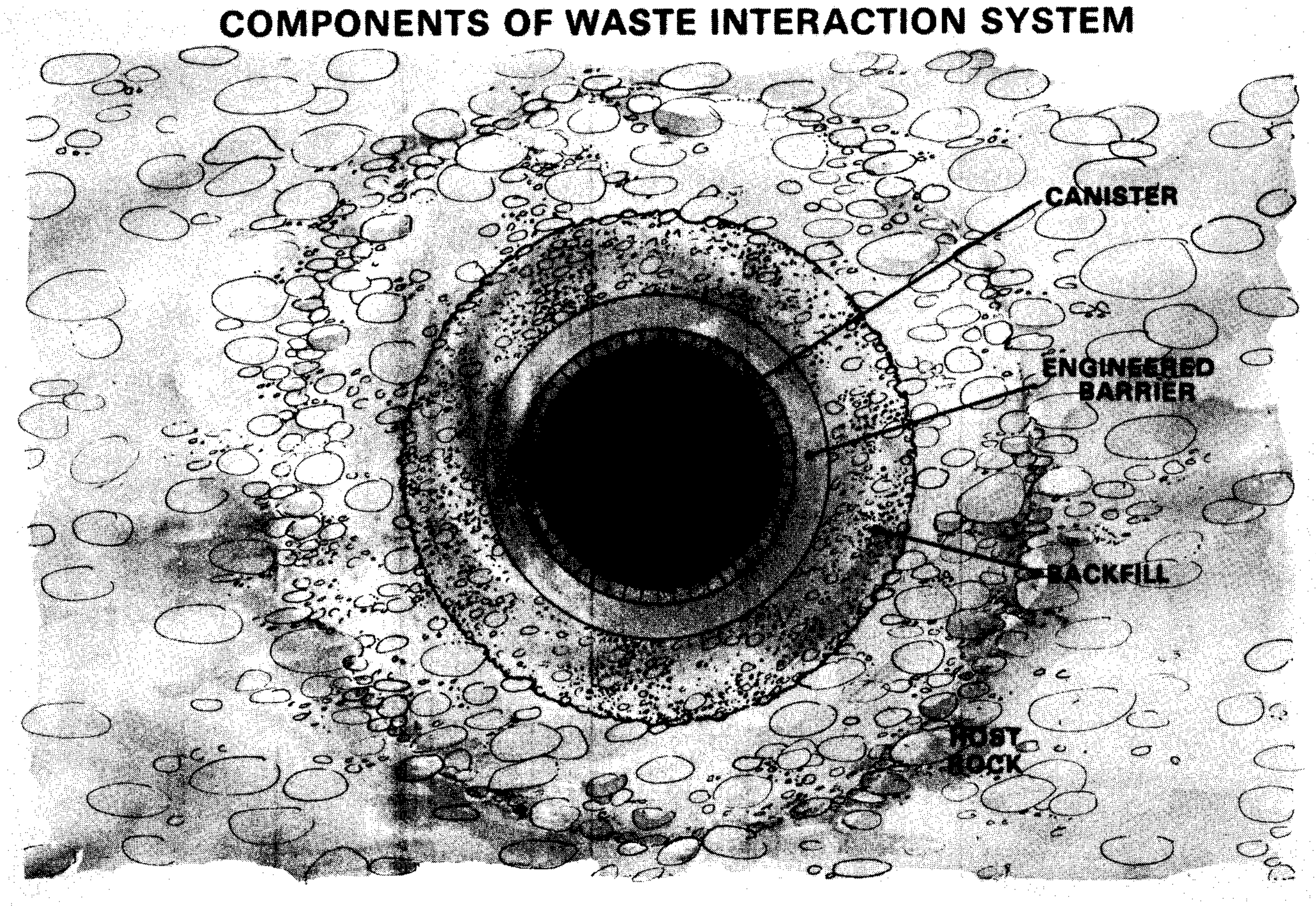

COMPONENTS OF WASTE INTERACTION SYSTEM

FIGURE 1-1. Components of Waste Interaction System.

2 BACKGROUND

2.1 REPORTING OF RESULTS

Leaching, as used here, is a term encompassing the many processes involved when a solid is placed in contact with an aqueous solution. Since nuclear wastes are complex solids, the interactions are not simply described, as undoubtedly several mechanisms are in operation at the same time. These mechanisms include diffusion, ion exchange, dissolution of the waste form matrix, surface resorption, and precipitation reactions. In the case of a waste package system, leaching studies must consider not only the waste form but the other components as well as the host rock and the geochemistry of its associated ground water.

A wide variety of methods and units have been applied to reporting results from leach testing. Results have been reported using the following methods:

- Leach or Release Rates (g/m^2 - day)
    1. Based on weight loss of the solid
    2. Based on elemental release as measured in the liquid corrected for losses such as on container walls
    3. Based on elemental release normalized to element content in the sample.
- Leach or Release Rates (g/day)
    1. Based on weight loss
    2. Based on elemental release
    3. Based on elemental release normalized to element content in the sample.
- Fractional Loss (percent)
    1. Based on weight loss
    2. Based on elemental release normalized to element content in the sample.
- Penetration (m/sec)
    1. Based on weight loss

2. Based on elemental release

3. Based on elemental release normalized to element content in the sample.

- Solution Concentration (μg/ml)

    1. Based on elemental release.

It is important to realize that the above methods have been generated over quite some time by researchers throughout the world striving toward many different objectives. Needless to say, this has greatly contributed to the confusion about "leaching" studies. Paramount for the needs of those involved in waste isolation programs aimed at licensing a repository is the ability to compare waste forms and provide input to source term modeling efforts. The Materials Characterization Center (MCC) has been established to standardize leaching procedures and reporting methods. The results will be a Materials Handbook of consistently taken and reported data.(1) The following units have been adopted as being the most useful for this purpose:(2,3)

- For static tests having no solution flow:

    1. Release value (g-waste form/m^2), based on a specific element normalized to element content in the sample
    2. Solution concentration (μg/ml)
    3. If a rate is to be expressed it should be derived by taking the slope (at a specified time) of the curve generated by release value (1 above) versus time.

- For dynamic tests, where the solution is changed or there is a flow of solution:

    1. Release value (g-waste form/m^2-day), based on a specific element normalized to element content in the sample
    2. Solution concentration (μg/ml).

Thus, both a solution concentration of the element in the leachant, and an element weight fraction (normalized) value or rate would be reported. The latter must include values for element sorption on the walls of the test container. Therefore, the leach or release data will represent the total material removed from the sample, and the solution concentration data will be only that which remained in the solution. It should be stated whether or not the samples were filtered. If filtered, the size of the filter paper should be included. Additionally, solution type, volume, and geometric sample surface area must be included with the data along with temperature, time, and pressure, if applicable. All results must have pH values reported with them. Reporting results in this manner will make them useful to the entire waste isolation community.

2.2 THE APPLICATION OF LEACHING STUDIES

Leaching studies have been under way at numerous laboratories for some time. This section is devoted to answering the question of how the results of these studies are used in the overall goal of performing safety assessments and eventually licensing a geologic repository.

The performance assessment of the package system, with the waste form as one of the elements of the package, is only one part of the performance assessment of the total waste isolation system, i.e., the package, the repository, and the surrounding geologic formations. Release of radionuclides, via aqueous solution contact, from the package to the repository environment and hence to an aquifer discharging to the biosphere, is the general process envisioned whereby humans could become exposed. Hence, a leaching and/or release test is appropriate for determining the potential consequences of such contact.

A number of studies have shown that retardation of radionuclide transport and other dispersive effects by the geologic environment through which the radionuclide moves, along with slow ground-water flow rates, is the major factor in limiting release to the biosphere.(4,5) However, if the leach rate from the waste form is low enough, it can become the rate-limiting step. One may envision situations, such as human intrusion into the repository, where leach rates from the waste form and release from the package system become increasingly important.

The application of results from leaching studies has progressed significantly from the time when the first performance assessments of geologic disposal gave no credit for the waste form or canister, as the integrity of the geologic formation was all that was deemed necessary. Either all the waste form radionuclide inventory was considered available for migration at the initiation of a repository breach or, for the case of salt, the waste form dissolved at the same rate as the geologic formation.

As a more conservative attitude became prevalent and as further studies on waste forms, canister materials, and engineered barriers began to gather and interpret data, a shift in the approach to isolation analysis gradually occurred. Emphasis was shifted towards looking at the entire system of engineered components and natural (geologic) components to do the job of containment.

At this point, some specific elemental release rates were factored into preliminary safety assessments(6) based on leaching data from studies of candidate waste form materials with simulated ground waters.

Further improvements in the waste form/solutions interactions data base have led to the incorporation in safety assessments of categories of element release, depending on whether or not the particular element was more likely to be a part of the matrix (solid-solution) or not. Also included was a temperature dependence on release, an attempt at deriving the surface area of the waste form to be exposed, and the effects of flow rate were incorporated by adding solubility limit constraints on the amounts of radionuclides released.(7)

At the present time those concerned with performance assessment are developing more detailed mathematical models of the package system to take into account more realistically the degradation of barriers other than just the waste form, that is, the canister and overpack, backfills, etc. However, the leach rate of the waste form remains an important and perhaps rate-limiting factor in the release rate of radionuclides from the package. It therefore remains an important factor in the source term for subsequent calculations of radionuclide transport to the biosphere and possible exposure to humans.

2.3 LEACH TESTING METHODS

The concept of predicting the amount and rates of release of radionuclides from waste forms in a geologic storage environment is complex. Safety assessments utilize this concept by incorporating a "source term" for radionuclides based on first, the release from the waste form via ground-water contact and subsequent interaction with surrounding engineered barriers, and second, the migration of the released radionuclide species to the biosphere via ground-water flow paths. The latter is the topic of a parallel ONWI document on migration. The present document will concentrate only on the first part of this source term.

How do components of this waste isolation system interact with each other to cause the release of radionuclides? A wide variety of possible interactions can be postulated. However, only a small number are reasonably probable and need to be considered in detail when evaluating waste forms. Two cases generally have been chosen for study that bound the responses of radionuclide release.

Case 1. In this case ground water directly contacts the waste form, short-circuiting the backfill/engineered barrier system, and then migrates through a fracture path in the host rock. As we will discuss later, this case has received most of the emphasis to date in order to gain knowledge of fundamental waste form-solution interactions.

Case 2. In this more realistic situation, ground water must penetrate or corrode the outer barriers before it contacts the waste form. Contact results in release of radionuclides which then must traverse the barriers before entering a host rock pathway to the environment. Because of the added barrier interactions, this case requires more attention to test design and to analytical detail in order to interpret the results. Although not the subject of this report, several studies are under way to assess waste package system interactions.(8,9)

One can see from this discussion that a single test will not cover the range of conditions presented in Cases 1 and 2. Thus, nuclear waste study programs have used a variety of procedures to gain data on radionuclide release and mechanistic understanding such that input can be provided for safety assessments in a timely fashion. Based on the premise that one should try to understand simple experiments first, binary experiments (Case 1) are performed using a combination of waste forms and solutions. The effects of temperature, solution composition, solution flow rate, radiation fields, and laboratory time are investigated to:

- Provide radionuclide release data
- Prioritize the effects of parameters
- Provide samples for surface analysis which will help the understanding of the formation of protective layers and their compositions
- Provide solutions for use in sorption-migration studies

- Provide insight into the design of more complex tests.

Leaching data for all waste forms are obtained in essentially the same manner. Tests fall under two broad categories, static and dynamic. In the static tests, the samples are immersed in the same leachate for the entire duration of the test and, if time periods are long enough, solubility limit data can also be obtained. These tests are conducted at temperatures both below and above the boiling temperature of the leachate. The higher temperature experiments must be pressurized and are conducted in an autoclave. Dynamic tests are those in which the original leachate does not stay in contact with the sample for the entire experiment. This condition can be met by having solution flow past the sample in a continuous manner or by a series of static tests in which the leachate is renewed at intervals. If the renewal rates are short compared to the time required to reach saturation, these tests can be reasonable simulations of continuous flowing tests.(10)

Most leaching results reported in the current literature utilize one of the following types of test:

1. Modified IAEA test
2. Static test
3. Single-pass, continuous-flow test.

2.3.1 Modified IAEA Leach Test

The International Atomic Energy Agency (IAEA) test's major feature is that the solution used is renewed on a preset schedule.(11) At the change times, the sample being studied is placed in a fresh volume of solution and the test is continued. Almost all investigators using the IAEA test have modified it to some extent, usually changing the schedule for solution renewal. In some cases the test has been modified by changing the longest leach time to one month to avoid sampling frequency effects of radionuclide release.

The various modified IAEA leach tests have the advantage that they are simple tests to perform, require little laboratory space, and are relatively easy to conduct in a hot-cell environment. The disadvantages are that they (1) require more effort to conduct than a static leach test because of the need to replenish the leach solution on a designated time schedule; (2) generate numerous leach solution samples, thus incurring higher analytical costs; and (3) do not correctly model probable ground-water flow conditions, primarily because of periodic leach solution replacement during the test (solution changes cause cyclic pH and solution concentrations, which in turn affect leaching). This makes interpretation of the data difficult vis-à-vis the geologic environment.

2.3.2 Static Test

Static tests investigate the effects of increasing radionuclide and matrix element concentration in the leachant as well as reabsorption reactions on radionuclide release rates. As the name implies, no sample agitation, solution flow, or solution replenishment is involved. To avoid potential difficulties with periodic removal of only a small leachate sample for the analyses, the tests are usually designed such that a series of replicates, started at the same time, are leached, with one replicate being sacrificed for each analysis.

The advantages of the static leach test are that it is the easiest test to conduct and simulates near-zero or very low ground-water flow in a repository. The static test also allows study of the approach to solubility limits for various radionuclides and matrix elements, which is important in determining thermodynamic solubility constraints. The test is also easily adopted to hot-cell environment operation and requires minimal work space. Possible problems when using plastic leach containers are solution loss, container material-leach solution interactions, and container degradation when running the tests for long times (>1 yr) at temperatures near 100 C. These problems can be overcome by utilizing welded gold or platinum capsules, but such tests become costly. Possibilities for improving the long-term aspects of the static test are to use Teflon containers or double containers.

For temperatures above 100 C, autoclaves are used for static tests. An advantage of autoclave tests is that they can simulate worst-case repository temperature and pressure conditions; and due to accelerated leaching at elevated temperatures, the tests are of shorter duration. Another advantage is that element solubility limits can be more rapidly reached at the higher temperatures. However, autoclave tests have several disadvantages. They are the most expensive of leach tests, cannot easily handle large numbers of samples, require more laboratory space than the other leach tests, and are not easily used in a hot-cell environment. The tests also require experienced personnel for operation and maintenance and special safety precautions.

For further details on static testing, the reader is referred to the literature.(2,3,12,13)

2.3.3 Single-Pass, Continuous-Flow Test

As discussed in the previous section, one needs the ability to describe radionuclide release under conditions where the solution flow sweeps accumulating reaction products from the surface of the waste form. Thus, the complement to the static test is one that accurately meters a solution as it passes a waste form sample.

Weed and Jackson(14) first devised the flow test concept in an attempt to reproduce these underground flow conditions in the laboratory and to assess realistically the stability of explosion melt glass, or candidate waste forms for nuclear waste disposal, to ground-water leaching and corrosion. Several parameters can be studied simultaneously with this type of experiment. Solution compositions ranging from distilled water to saturated salt brine and temperatures of 25 and 75 C have been used successfully. The flow rate can be varied over a wide range of values that are commonly found in natural aquifers, and a variety of waste forms can also be studied.

One advantage of the flowing test is the close analogy to an actual flooded repository where ground water would slowly flow past the waste because of the natural hydraulic gradient. Peristaltic pumps and tubing are available that will deliver volume flow rates typical of observed underground water velocities.(14)

Another advantage is the ease of obtaining data regarding flow rate effects on leach rate. Flow rate is an important parameter because it is related to the total volume of water which contacts the waste form and may control the leach rate at which radionuclides can be leached from the waste form. Because candidate repositories will likely have the potential to experience a variety of ground-water velocity regimes, an understanding of the effect of flow rate on leach rate could become a key factor in evaluating repository performance.

The primary disadvantages of the flow test method are increased complexity and expense when compared to the modified IAEA and static leach tests. Pumps, hoses, and specially constructed cells are required. The assembly, monitoring, and maintenance of the test require experienced personnel. The test demands more laboratory space than the modified IAEA or static leach test; and, like the autoclave test, the test is not easily adaptable to a hot-cell environment.

3 STATUS OF GLASS AND SPENT FUEL LEACHING

Most waste form-aqueous solution interactions involve both the removal of elements from and the introduction of elements into the sample by the contacting leachate solution. Therefore, to more fully understand the interactions which are occurring so that long-term predictive models can be developed, both solution composition and solid state surface analyses must be performed. The solution analysis allows a determination to be made of what has been removed from the sample but does not yield much information about how elemental removal occurred. This type of information is obtained from analyses of the solid sample. Surface analyses can be utilized to determine the extent and type of layer development on sample surfaces. In addition to surface chemistry, surface analyses techniques, when combined with ion milling, yield valuable information about elemental depletion profiles from the sample.

One of the ever-present difficulties in leaching experiments is the container. One must be sure that the container material is chemically inert and does not sorb elements in the leachate, which might adversely affect the leaching results. The effect can be reduced by proper choice of container material and by minimizing the container surface area exposed to the leachate.

In the case of leaching tests which result in significant reaction and elemental removal, precipitation must be considered. If precipitates occur (can be colloidal in nature), elements can attach to these precipitates, particularly if they are silicates, and cause erroneous results to be obtained for solubility limits and leaching characteristics if the leachates are not properly filtered.

There are numerous waste forms which are being considered for containment of radioactive waste. These include several forms of crystalline ceramic materials, coatings of various types, glasses, and spent fuel itself. Currently, the largest body of data has been generated for glasses and spent fuel, and therefore these two wastes forms are the focus of this paper.

3.1 GLASS

The interactions of glass with aqueous solutions have been actively investigated for more than 20 years. Until recently, the majority of experiments were conducted on relatively simple commercial or naturally occurring silicate glasses.(15-26) Consequently, most theories and models for glass-water interactions are based on simple silicate glasses.(15-18,27,28) Currently, however, because borosilicate glass is a candidate material for containment of radioactive waste, many investigations have been conducted on interactions of the more complex borosilicate waste glasses with aqueous solutions.(29-38) A typical waste containment glass has 30 or more elements (see Table 3-1) and can react with aqueous solutions in a manner quite different from that of simple silicate glasses. Additionally, glasses containing fully radioactive waste must be handled in a hot cell, which is expensive and limits the type, quality, and quantity of analyses which can be performed on the samples. Therefore, most investigations are performed on glasses containing simulated waste, that is, nonradioactive elemental substitutions for the radioactive elements where possible and substitution of rare earths for actinides. In some cases, actinides have been doped into the glass at expected levels, which necessitates that experiments be conducted in glove boxes and somewhat restricts surface analyses of the samples.

When a glass is exposed to an aqueous solution, the elements removed from glass by the solution typically follow a time dependence similar to that described in Figure 3-1. In the initial time period, up to time t, the leach rate begins rapidly and decreases with time, curve segment A. The data represented by this curve segment usually are linear when plotted versus square root of time, a fact which has led numerous investigators to attribute this time period of leaching to diffusion-controlled processes.(15,17,18,20,21,27,28) For times greater than t, elemental removal can have the time dependence described by either curve B, C, or D. For most elements in simple silicate glasses and many elements in more complex borosilicate waste glasses, curve segment B is followed. This is partially true because of the relatively short duration of typical leaching tests or when large volumes of water are used. If leaching characteristics are described by curve B, elemental removal is linear with time (constant leach rate), and has generally been attributed to corrosion or dissolution of the glass matrix.(15,17,18,21,27,28) If the glass is exposed to the same leachate for long periods of time or an element has a very low solubility limit, then curve C may result. This represents a steady state or apparent equilibrium value for the maximum concentration of a particular element which will stay in solution under the experimental conditions. When conditions change during the course of an experiment, as occurs

TABLE 3-1. Nominal Compositions of Typical Waste Glasses. (from Ref. 67)

Component		Glass Composition, wt %		
		76-68 PW-8a-1	77-107 PW-9-1	77-260 PW-7c-1
Glass Frit	Al_2O_3			2.0
	B_2O_3	9.5	13.0	9.0
	CaO	2.0	2.0	1.0
	CuO			3.0
	K_2O		4.0	2.0
	Na_2O	7.5	2.0	8.0
	SiO_2	40.0	38.0	36.0
	TiO_2	3.0	3.0	6.0
	ZnO	5.0	5.0	
		67.0	67.0	67.0
Waste	Ag_2O	0.03	0.05	0.02
	BaO	0.56	1.13	0.55
	CdO	0.03	0.08	0.03
	CoO	0.11	0.20	0.10
	Cr_2O_3	0.41	0.21	0.02
	Cs_2O	1.02	1.98	0.78
	Fe_2O_3	9.68	0.90	1.19
	Cd_2O_3			10.14
	MnO_2			0.11
	MoO_3	2.27	4.41	1.92
	Na_2O	5.00	3.47	3.14
	NiO	0.52	0.16	0.31
	P_2O_5	0.48	0.40	2.36
	Rb_2O	0.13	0.25	0.11
	RE(a)	4.76	9.24	3.84
	RuO_2	1.06	2.20	0.85
	SrO	0.38	0.72	0.29
	TeO_2	0.25	0.50	0.22
	U_3O_8(b)	4.54	3.80	5.40
	ZrO_2	1.76	3.30	1.68
		33.00	33.00	33.00
		100.00	100.00	100.00

(a) A commercial rare earth mixture having the nominal composition in wt %. 0.2, H_2O_3; 24.0, La_2O_3; 48.0, CeO_2; 5.0, Pr_6O_{11}; 17.0, Nd_2O_3; 3.0, Sm_2O_3; 0.8, Eu_2O_3; and 2.0, Gd_2O_3.

(b) U_3O_8 prepared from depleted uranium.

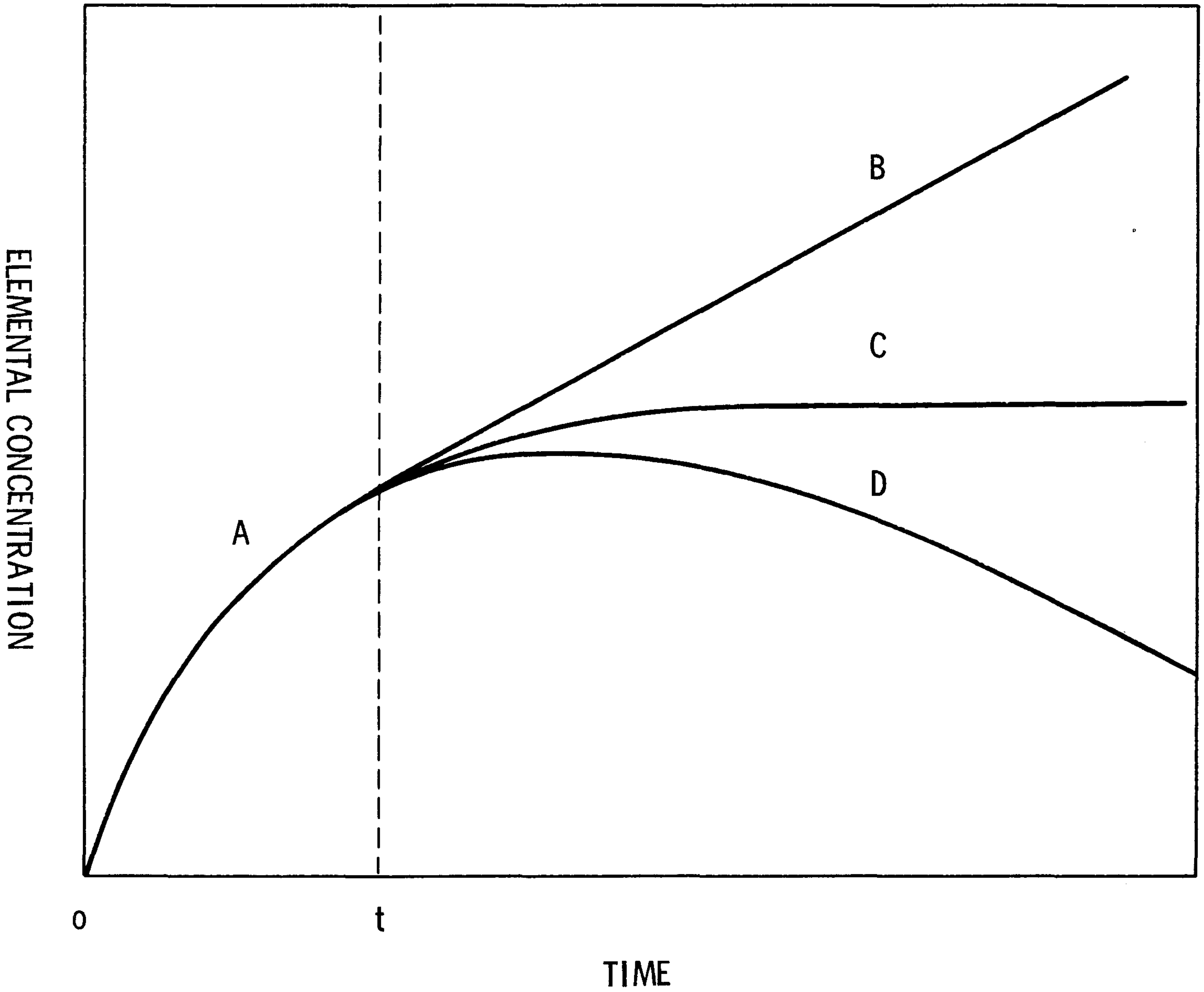


FIGURE 3-1. Schematic Diagram of the Time Dependencies of Elemental Concentrations in the Leachate.

in static tests (changing pH and solution concentrations), then time dependence of elemental concentrations in the leachate can be described by curve D for certain elements. This decrease in solution concentration can be attributed to precipitation and/or sorption of elements on sample surfaces.

Any process which enhances leaching, such as increasing temperature, using a less durable glass composition, or exposure to flowing conditions, results in a decreased contribution from segment A (smaller t). Additionally, if a flowing test is sufficiently rapid, time dependence described by curves C and D will not exist for any of the elements.

The variation of leach rate with time, as depicted by curve A in Figure 3-1, has been shown, for a natural glass, to be the result of fines adhered to the leach sample surface.(16) When the fines were removed from the sample, only a time dependence described by curve segment B remained. The nonlinear portion of the curve, segment A, was caused by a more rapid reaction of the fine (large surface area) particles with water. Therefore, care should be taken not to automatically assume a diffusion-controlled process because the leaching data appear to have a square root of time dependence.

Solution data from a static leach test on a typical borosilicate waste glass (PNL 76-68) are illustrated in Figure 3-2. As can be seen, time-dependence characteristics of curves A, B, and D in Figure 3-1 exist for the different elements. The experiment was not conducted for long enough time periods to observe characteristics represented by curve C in Figure 3-1. Leach tests conducted under normal laboratory flowing conditions typically have only linear time-dependent elemental removal characterized by curve B in Figure 3-1.(39,40)

Solution analyses of the leachate yield only part of the information about glass-water interactions. Analyses of the reaction layer which has developed on the solid sample produce a greater understanding of elemental release mechanisms. Elemental depth profiles have been obtained by progressive HF acid dissolution and analyses of the reaction layer.(41,42) However, this can lead to selective removal of alkali ions.(43) A better approach is the use of relatively new surface analytical techniques such as ESCA (electron spectroscopy for chemical analysis) in combination with ion milling to obtain elemental concentration profiles in the reaction layer. A recent review of surface analytical techniques and their limitations is given elsewhere.(43)

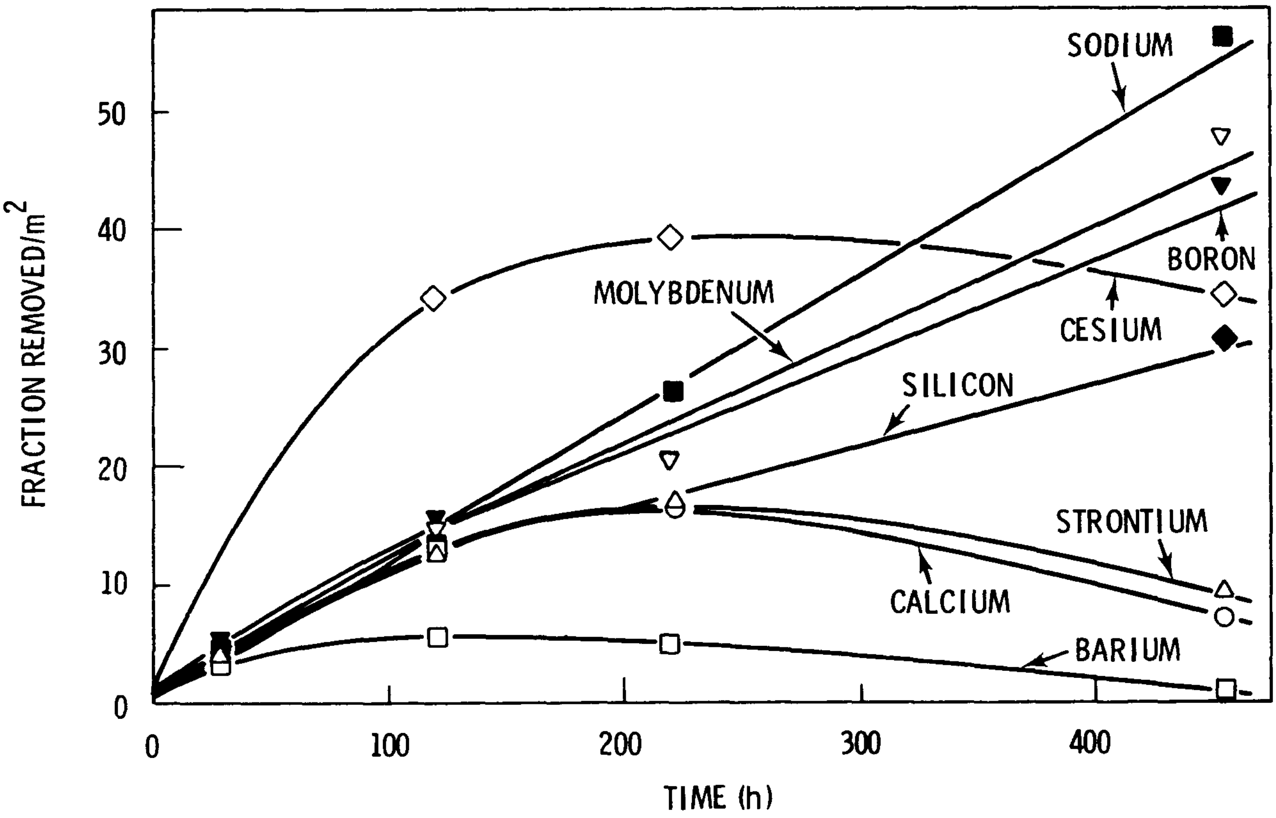


FIGURE 3-2. Fraction of Original Elemental Concentration Removed by Leaching in Distilled Water per Unit Surface Area of Sample for PNL 76-68 Glass at 89 C, with a Surface Area-to-Solution Volume Ratio of 10 m^{-1}. (Ref. 30)

Elemental concentration profiles in the reaction layer which forms on the glass surface as a result of interactions with water can be described by one of the curves illustrated in Figure 3-3. The solid curves (A and B) and dashed curves (C and D) represent element concentration profiles which are, respectively, more concentrated and less concentrated than in the bulk unreacted glass.

Concentration profiles represented by curve A are obtained for elements which react less than the glass matrix elements with water. Therefore, as the matrix elements are leached away, these less soluble elements build up concentrations larger than originally existed. This concentration is enhanced to the depth where matrix elements have been removed. Concentration profiles of this type are seen quite frequently for heavy metals, rare earths, and actinides in borosilicate waste glasses but are seldom observed on simple silicate

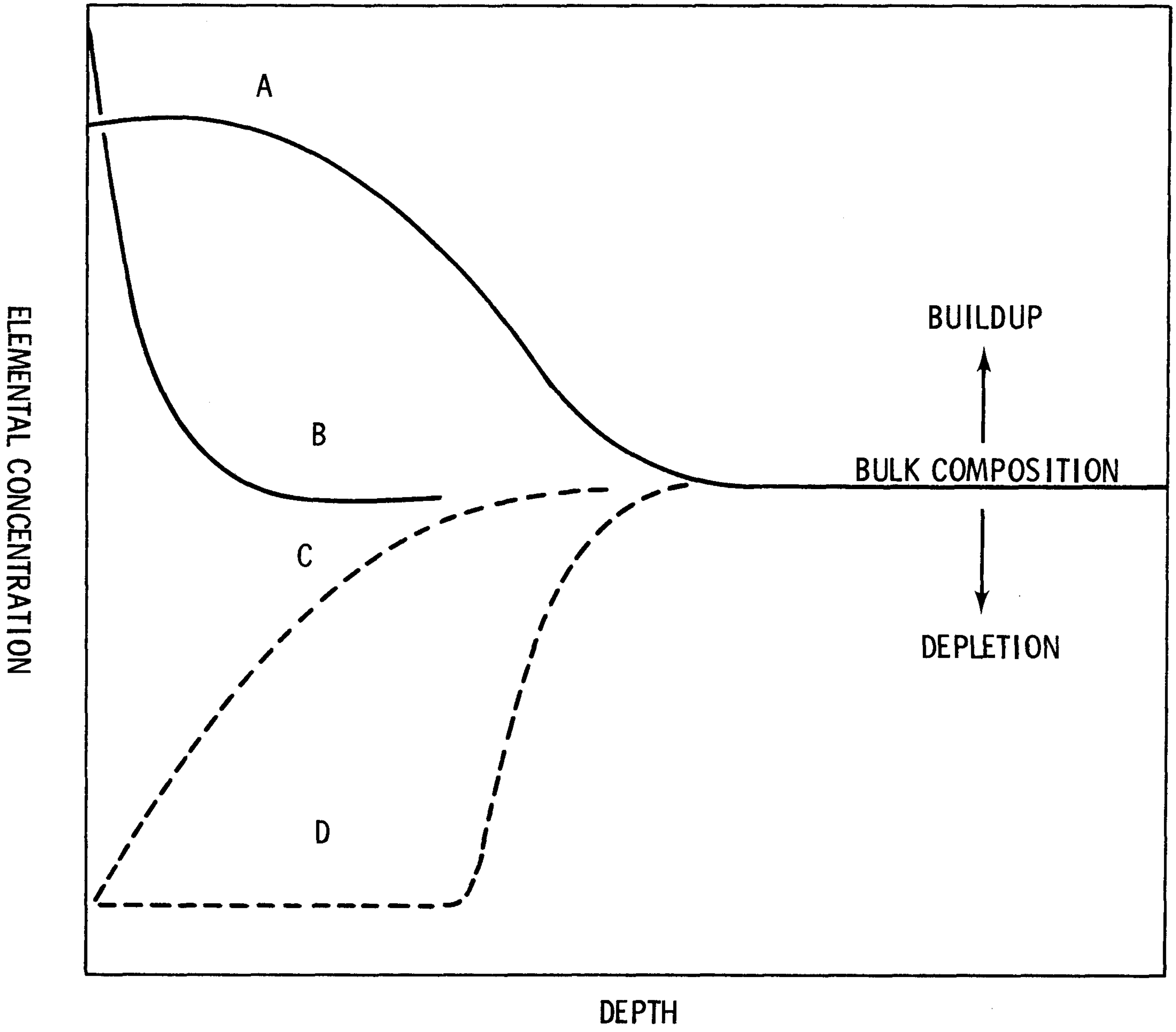


FIGURE 3-3. Schematic Diagram of Elemental Depth Concentration Profiles Through a Reaction Layer Resulting from Leaching of a Solid Sample.

glasses. If elements precipitate or sorb on the glass surface (elements can be from some external source other than the glass), then a profile described by curve B can result. This profile is typically restricted to regions near the surface, although some diffusion into the reaction layer is possible which would broaden the profile.

Elements which are leached at comparable or more rapid rates than the matrix elements typically have concentration profiles similar to either curve C or D in Figure 3-3. Profiles similar to curve C are the result of ion exchange of elements in the glass with species from the water (H^+ or H_3O^+, for example. It is in essence a diffusion profile. Matrix elements often have concentrated profiles similar to curve C. This is the result of the previously mentioned ion exchange of elements in the glass with water species which in turn interact with and break up the glass matrix.(15,20,27) Therefore, the matrix elemental concentration profiles are similar in shape and closely related to those elemental profiles which result from ion exchange with water species. As the glass-water interaction progresses, enough matrix breakup occurs to allow ionic species to move very rapidly through the highly reacted portion of the interaction zone. Thus, curve D in Figure 3-3 results. Curve C usually tends toward curve D with time. Diffusion of ionic species through the initial region of curve D occurs several orders of magnitude more rapidly than through the bulk glass.(20) Leaching, for elements described by curve D, is essentially occurring as if the highly reacted region of the interaction zone were not there.

For example, elemental concentration profiles for a leached PNL 76-68 borosilicate waste glass are given in Figure 3-4. These profiles were generated by a combination of ESCA surface analysis and ion milling. As can be seen, concentration profiles of the type described by curves A, B, and D in Figure 3-3 are present. If the leached sample had been analyzed after a shorter time exposure to water or had been leached at a lower temperature, then concentration profiles of the type described by curve C in Figure 3-3 would have been present.

Analyses of glass surfaces leached under more extreme conditions, i.e., higher temperatures or longer times, must be conducted in other ways. If the reaction layer becomes very thick (many microns), then sputter profiling is not practical and can lead to erroneous results due to large-scale sputtering and to surface analyses at the bottom of a deep crater. These highly reacted

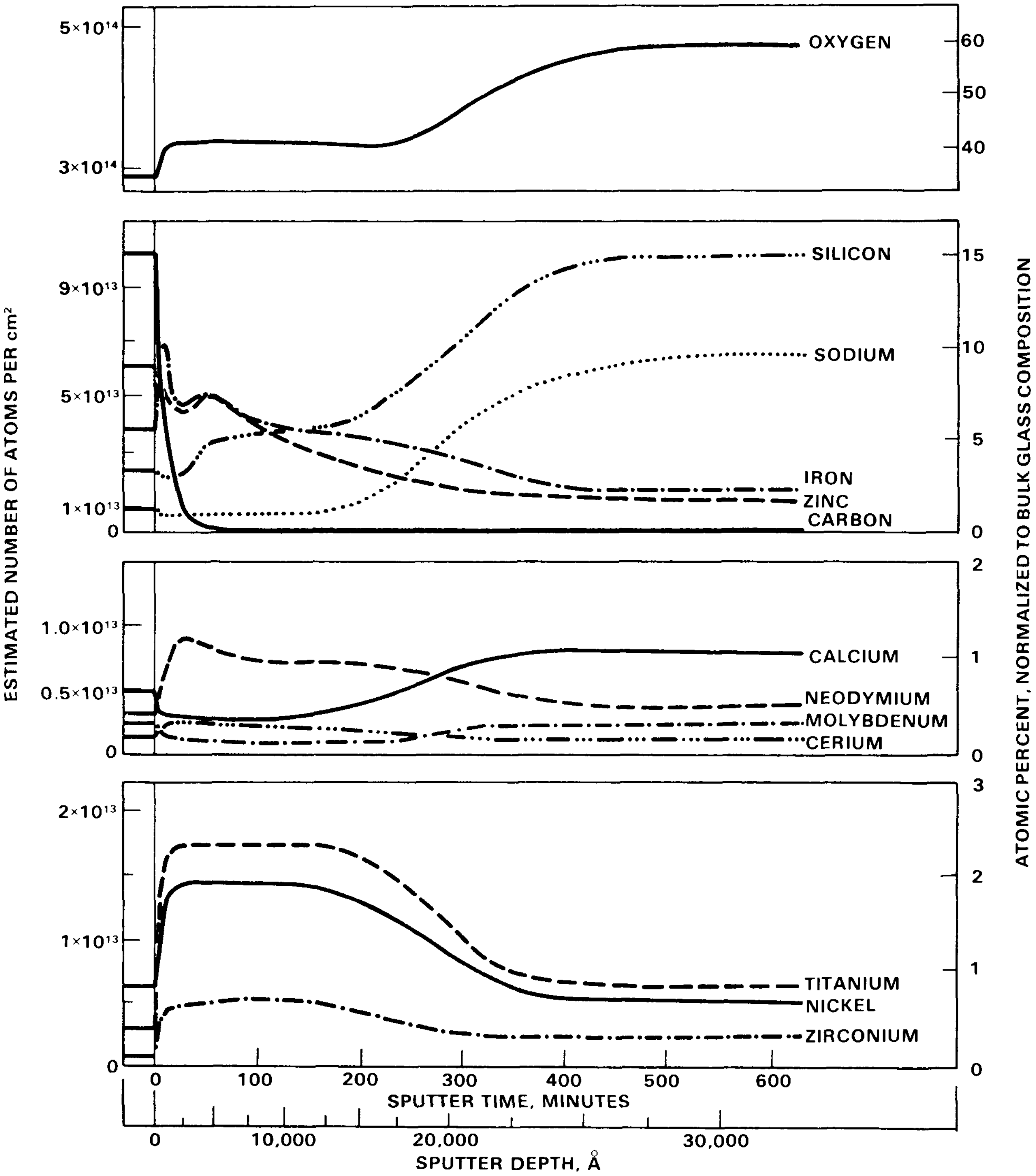


FIGURE 3-4. Elemental Concentration Profiles Through the Reaction Layer of a PNL 76-68 Glass Sample Exposed to 90 C Distilled Water for 14 Days with a Sample Surface Area-to-Solution Volume Ratio of 10 m^{-1}. (Ref. 43)

glass surfaces are best analyzed by evaluating their cross sections with an ion microprobe or scanning electron microscope (SEM) used in conjunction with energy dispersive X-ray analysis (EDAX). These profiles are interpreted in basically the same manner as those previously described. However, the reaction layers can become more complex with zone formations, which makes interpretation difficult.

The following discussions will concentrate primarily on waste glasses but will utilize data from the relatively simple silicate systems where beneficial or necessary for purposes of comparison or understanding. Although it is realized that when glass interacts with aqueous solutions many effects are simultaneously occurring and are interrelated, these effects will be discussed separately, as much as is possible, in an attempt to describe what is known about each area.

3.1.1 pH and Eh Effects

The effects of pH on elemental leach rates from glasses is well documented.(15,17,18,44,45) However, an understanding of why these effects occur is lacking, particularly for the more complex borosilicate waste glasses.

The pH dependence of leach rates based on silicon analyses or sample weight loss can be described by the schematic curves shown in Figure 3-5. (15,44) Curve A represents simple silicate glasses or fused silica, and curve B represents borosilicate waste glasses. As can be seen, there is a fundamental difference in the behavior of the two types of glasses. The simple silicate glasses are durable in the acid region but suffer large-scale glass matrix attack in the basic pH region. For fused silica, the matrix attack becomes significant at pH values above 8.5. The addition of alkali to the glass results in a decrease of the pH value where rapid matrix attack begins. Alkali ion leach rates from simple silicate glasses have just the opposite pH dependence.(15) They leach rapidly in acid pH solution but slowly in basic solutions. This is because ion exchange between the alkali ions and a positively charged water species must occur for alkali ion removal.

The borosilicate waste glasses exhibit enhanced durability in basic pH ranges but have poor acid resistance (curve B in Figure 3-5). The pH-independent region (high-durability region) is between pH values of 5 and 10.(44) Waste glasses contain many elements, most of which are more soluble in acids than in bases. Other waste glass elements exhibit high leach rates

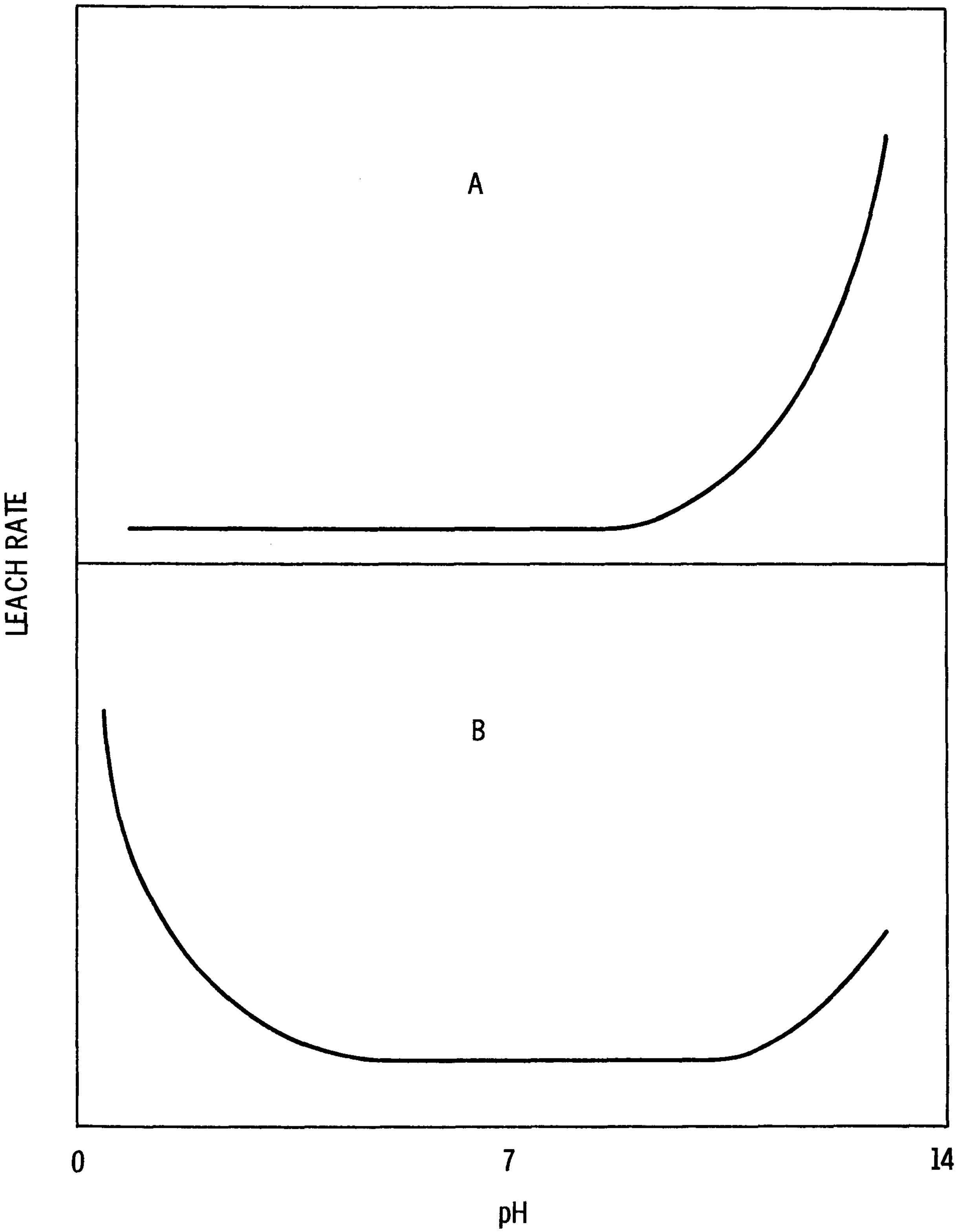


FIGURE 3-5. Schematic Diagram of pH Dependence of the Leach Rate for Simple Silicate (A) and Complex Borosilicate (B) Glasses.

in acids, but most of them have low leach rates in basic solutions.(46) Therefore, it seems likely that in the acid pH range, the silica portion of the matrix breaks up as a result of large-scale removal of most of the other elements. It has been demonstrated that rare earths make glasses more resistant to basic attack.(20) Since simulated waste glasses contain rare earths, this may be partially responsible for the increased durability of waste glasses in basic pH solutions.

The pH of natural waters ranges between 2 and 10; most ground water, however, lies in the more restricted pH range of 5.5 to 8.(47) Certain salt brines, when heated, can achieve pH values of 3, which would not be desirable and would necessitate the use of buffers. In a static or slow-flow situation, a glass will control its own pH, due to reactions with the water, unless the water is highly buffered or has a very large volume exposed to the glass.

The oxidation potential of ground water, usually expressed as Eh, can decrease with depth in the earth depending upon geochemical conditions. Thus, at proposed repository depths, leaching may take place under reducing conditions. The leach rate of elements which exist in more than one valence state can be influenced by the Eh of the leaching solution. Important waste radionuclides that fall in this category are ^{99}Tc and most of the actinides. However, essentially all of the leach test data on glass reported in the literature have been obtained in air-saturated solutions. One attempt has been made to leach actinide doped glasses in degassed water (approximately 1 ppm O_2).(48) A decrease in leach rate for the actinide elements investigated was generally observed.

3.1.2 Temperature Effects

Most leaching data have been generated at temperatures of 100 C or less. Many of these data are of the weight loss type which only gives gross indications of mechanisms. There are many reactions occurring simultaneously during glass-water interactions, and a temperature dependence exists for each reaction. It is possible that many of these processes have similar temperature dependencies; however, there is no current method to isolate and measure each process separately. Therefore, activation energies determined for leaching are a combination of several activation energies, one for each related process occurring. However, plots of log leach rate versus reciprocal temperature usually are linear over the experimental temperature span. Additionally, leaching mechanisms may be changing with time. This is particularly true if conditions are varying (for example pH) with time. Activation energies determined at different time periods for the same glass have yielded 7 kcal/mole initially and 14 kcal/mole for longer periods of time.(49) These results are presumably due to changes in leaching mechanisms with time. The temperature dependencies of leaching should be determined with long-time leaching data.

Activation energies have been reported by many researchers(49-51) and vary from 7 to 22 kcal/mole for the glasses investigated. There is not a large difference in temperature dependencies for leaching in various simulated ground waters. Several of the elements from a borosilicate waste glass with leach rates equal to or faster than silicon have been found to have the same temperature dependence of leaching.(52) Presumably the mechanisms of release are similar or the same. It is important not to extrapolate accelerated high-temperature results to lower temperatures for predictive purposes until it has been verified that a mechanism change does not occur.

3.1.3 Leachate Composition Effects

The addition of certain elements such as aluminum or calcium to distilled water has been shown to cause a reduction in leaching of glass.(53-56) Many elements, when in an aqueous solution, can react with the glass surface to alter its surface charge(57-58) and therefore affect the interactions which are occurring with water. Leachate compositions can modify the pH and in turn the leaching. Variations in aqueous solution compositions affect leaching differently for individual elements. Solutions of high ionic strength, such as salt water, typically enhance the removal of alkali and alkaline earth ions from glass,(30) while leachates containing complexing anions can enhance actinide removal from glass.(34)

Many investigators have reported the effects of simulated ground waters on elemental release from borosilicate waste glasses.(29,32-38) The magnitude of the effect is somewhat element-dependent, but the general conclusions are all the same, i.e., the various simulated ground waters have a small effect compared to pH and temperature. The variation in leaching for all simulated ground waters investigated falls within one order of magnitude. Typical results showing this effect are given in Figure 3-6. This result is from an IAEA dynamic test at 22 C for ^{237}Np. As can be seen, the effect is small, with the largest release occurring in the sodium bicarbonate solution. This result is typical for all of the actinides in waste glass.

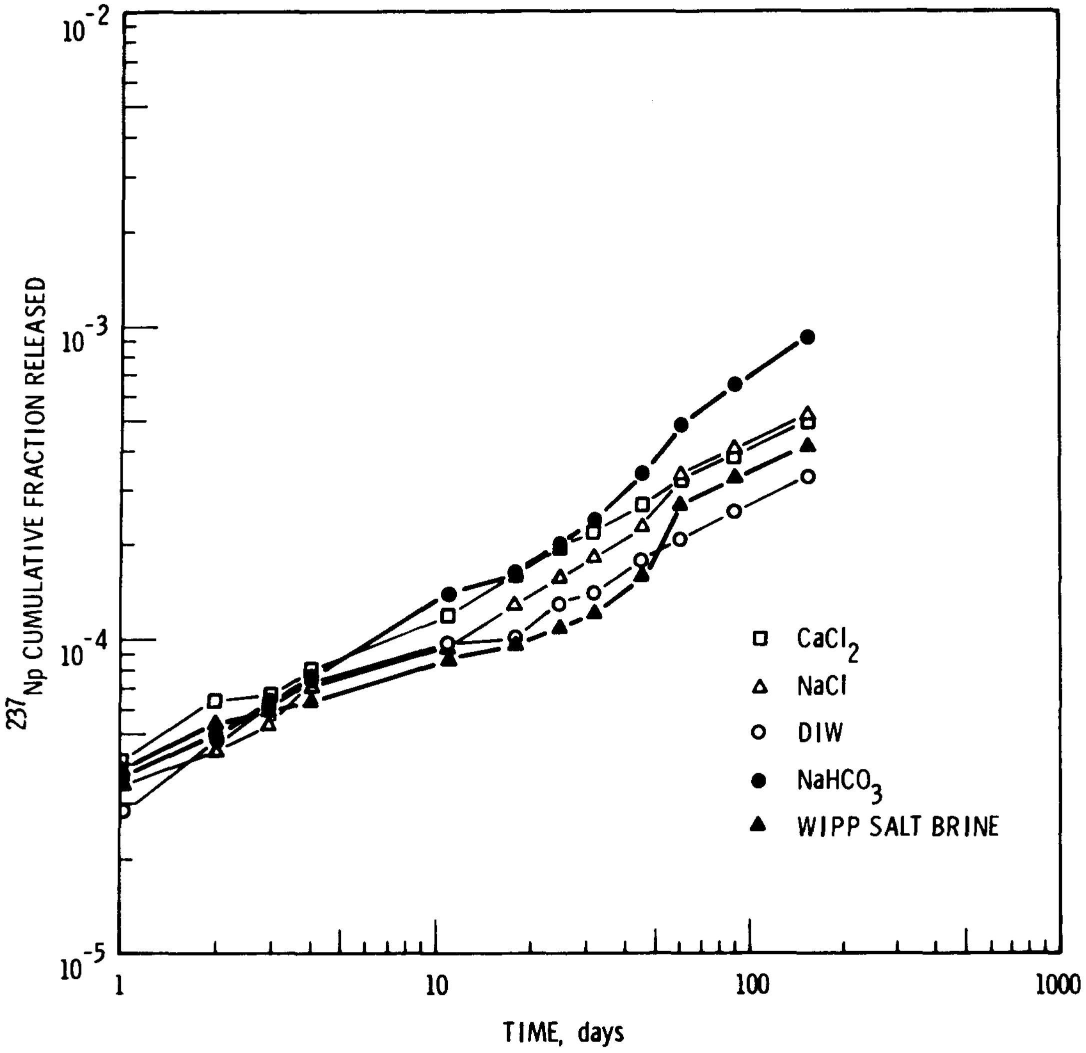


FIGURE 3-6. The Effect of Simulated Ground-Water Compositions on the Time Dependence of Cumulative Fraction of ^{237}Np Released from PNL 76-68 Utilizing an IAEA Leach Test at 22 C. (Ref. 34)

3.1.4 Radiation Effects

A glass which contains radioactive waste is exposed to continuous radiation from the waste itself. The largest amount of damage to the glass results from alpha decay, primarily from the recoil nucleus.(59) Accelerated testing of this alpha decay-related damage has been conducted by doping glasses with short-lived actinide isotopes, ^{238}Pu or ^{244}Cm, and allowing damage to occur by self-radiation.(44,59,60) Leaching these glasses as a function of accumulated dose has shown only a minor effect resulting from alpha decay-related radiation damage (see Figure 3-7 as an example). Alpha recoil damage has also been simulated by charge particle irradiations.(61) The premise is that low-energy lead ions simulate recoil nuclei generated by alpha decay. Leaching results on glasses damaged in this manner indicate a threshold damage level above which rapid leaching occurs.

This is in contrast to the results obtained from self-irradiation experiments. It must be realized that low-energy ions only damage the glass to a depth of a few hundred angstroms, and therefore leaching results are based on extremely near-surface phenomena which may not be representative. The effect of surface roughening due to ion irradiations and its effect on leaching have not been addressed. Therefore, it seems that self-radiation experiments are more realistic, but one cannot completely discount the charged particle simulations. More research needs to be conducted to clarify the apparent discrepancies between these two acceleration techniques.

Another radiation-induced change which may affect leaching is the transmutation of the fission products. The two main sources of transmutations are the intermediate-lived fission products ^{137}Cs and ^{90}Sr, which transmute to ^{137}Ba and ^{90}Zr, respectively. Transmutations can involve valence changes and major changes in atomic radii. The question is whether or not these transmutations affect elemental release from the glass. There are currently experiments under way to evaluate the effects of transmutations on leaching. However, no results are currently available.

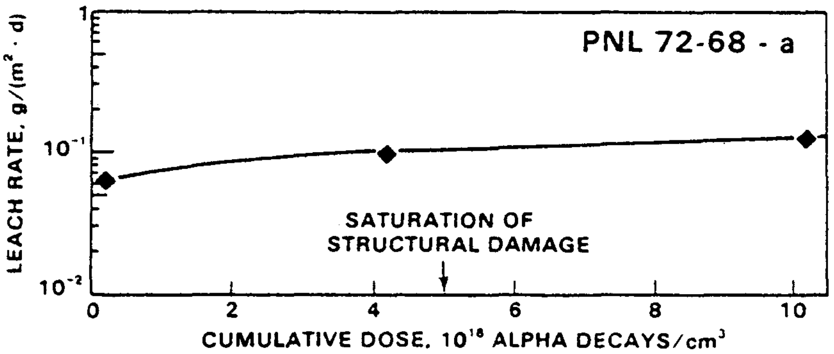


FIGURE 3-7. The Effect of Radiation Damage on Leach Rate, Soxhlet Test Leachability of ^{244}Cm-Doped PNL 76-68, a High-Level Waste Glass. (Ref. 59)

When a waste glass is in contact with an aqueous solution, radiation from the glass can cause changes in the chemistry of the solution. These changes can in turn have a significant effect on the leaching of the glass. Radiolysis of water can be caused by alpha, beta, or gamma radiation from the waste containment material.(62-65)

If the leachate contains nitrogen, nitric acid is generated as a radiolysis product.(62-64) This can cause rapid attack of the glass resulting in greatly enhanced leaching (See Table 3-2). Experiments where nitrogen is excluded show that leaching is still enhanced due to increased interactions by other radiolysis products in the aqueous solution.(62) This enhancement is strongest at lower temperatures and is minimal above 90 C.(66)

If real ground waters contain nitrogen, then radiolysis effects can be significant (an order of magnitude or larger increase in leaching). If nitrogen is not present, leaching of the glass matrix elements will not be enhanced at expected repository temperatures. However, the radiolysis of water can result in an oxidizing environment(65) which greatly enhances solubility and leaching of the actinide elements.

3.1.5 Solubility Effects

Amorphous materials are metastable and, therefore, cannot exhibit true thermodynamic solubility limits. However, because the kinetics for transformation to more stable states are slow for most glasses at reasonable temperatures, apparent solubility limits exist. These are apparently constant elemental concentrations in solution which is in contact with the glass. Investigations of solubilities of matrix elements(67) and actinide elements(68) have been conducted in demineralized water for borosilicate waste glasses. Additionally, much literature exists for amorphous silicon solubility limits.(69-71)

The apparent solubility limits determined from silicon concentrations in demineralized water for three borosilicate waste glasses(67) do not reach the values reported for amorphous silica(70) even after 1 year exposure time. Furthermore, some elements such as sodium and potassium do not reach saturation levels at 1 year. However, most elements in borosilicate waste glasses reach an apparent solubility limit within 3 months at 35 C with somewhat shorter time periods required at higher temperatures.

TABLE 3-2. Comparison of Gamma-Irradiated[(a)] and Unirradiated Leaching of PNL 76-68 Glass in Demineralized Water With a Sample Surface Area-to-Solution Volume Ratio of 10 m^{-1}.

Element	50 C γ-irr 5 Days	50 C no γ-irr 5 Days	90 C γ-irr 13 Days	90 C no γ-irr 13 Days
Na	5.0[(b)]	1.8	130.0	18.5
Cs	---	0.13	---	2.2
Ca	0.80	0.18	7.8	1.0
Ba	0.19	0.03	0.8	0.1
Sr	0.14	0.03	1.4	0.2
Si	6.5	1.44	177.1	21.0
B	1.1	0.26	31.3	4.5
Mo	0.1	0.13	7.2	2.6
Zn	2.0	0.17	37.6	0.09
pH	5.7/3.3	5.7/7.2	5.7/4.6	5.7/8.5

(a) Dose rate was 2.4 x 10^6 R/h.
(b) Parts per millon by weight.

The actinide elements have very low solubility limits compared to glass matrix elements and therefore reach them rather quickly. At room temperature, plutonium and neptunium leached fron PNL 76-68 glass reach saturation concentrations in approximately 5 days.(68) This concentration is identical to that observed for crystalline PuO_2 and NpO_2, respectively, indicating that the solubility limits of these actinides in PNL 76-68 glass are the same as, or are controlled by, PuO_2 and NpO_2. Thermodynamic data are known for these oxides and, therefore, if they are controlling the solubility, then long-term predictions of actinide concentrations in solution can be made with confidence. An example of the similarity of solubility limit data from PuO_2 and plutonium-doped glass is given in Figure 3-8.

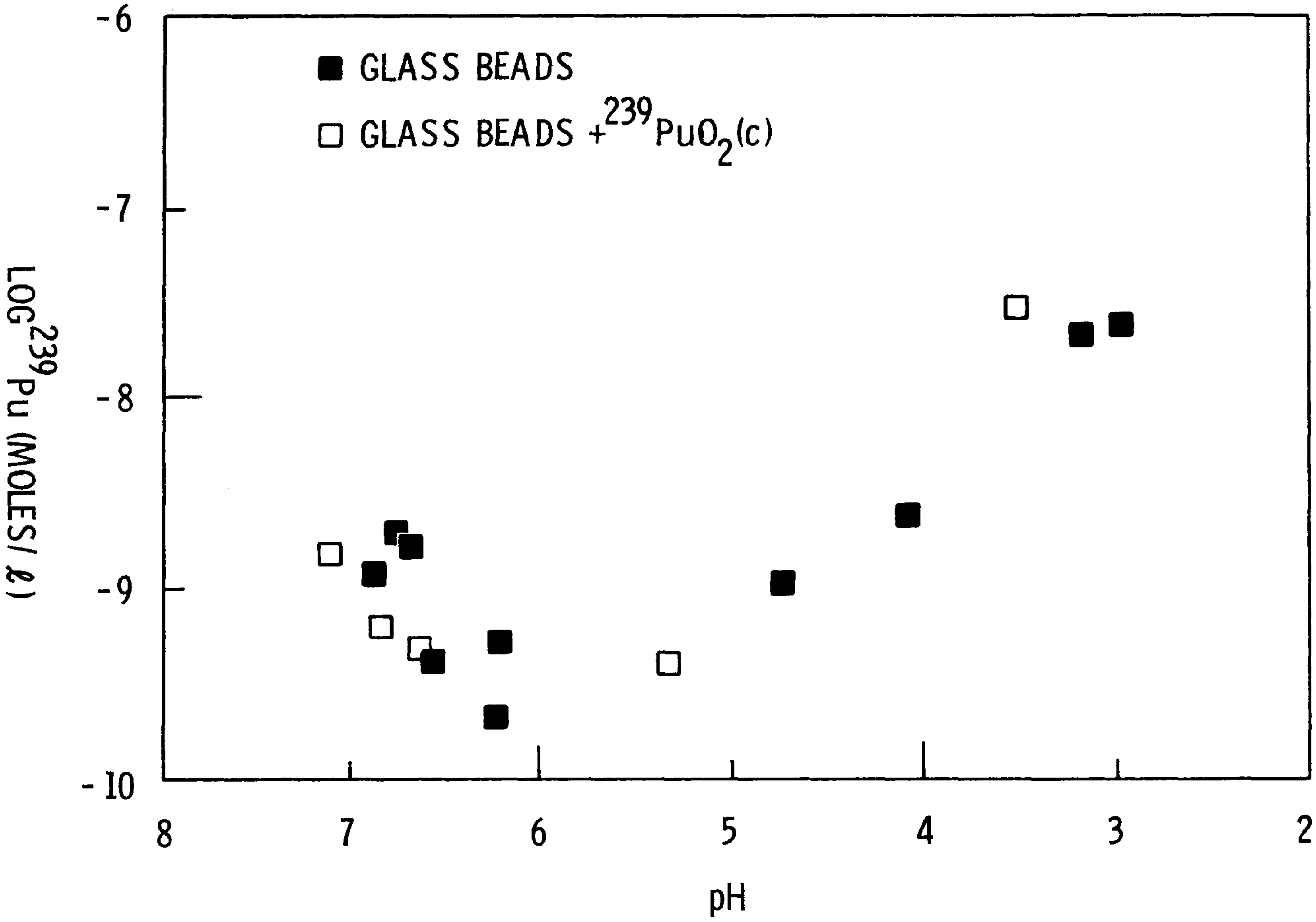


FIGURE 3-8. Solubility of Crushed Pu-Doped PNL 76-68 Glass Beads [With and Without the Addition of ^{239}PuO$_2$(c)] in 0.0015 M CaCl$_2$ Solutions Containing Quinhydrone. (Ref. 68)

3.1.6 Dynamic Leaching Effects

When the leachate is renewed during the time glass-water interactions are occurring, it is called a dynamic leach test. The major differences between leaching in dynamic and static tests is that saturation effects do not typically occur if the leachate renewal rate is frequent enough. Therefore, solution concentration curves from flowing tests normally have only linear time dependencies (described by curve B in Figure 3-1).(39,40) There is usually no square root of time dependency (curve A in Figure 3-1), as occurs in static tests. The effect of increasing flow rate is to enhance elemental removal rates,(39,40) particularly at temperatures above 25 C. The elements with lowest solubility limits and/or leach rates seem to be affected the most. Therefore, as the flow rate increases, the elemental leach rates all approach the same value and congruent dissolution.(40)

3.1.7 Mechanism and Models

When a glass interacts with an aqueous solution, many reactions are occurring simultaneously. There are elements being removed from the glass by ion exchange with positively charged water species (H^+ or H_3O^+, for example) and by matrix breakup due to hydroxyl ion attack. Therefore, the glass is both losing and gaining ions in its interactions with water. Earlier work reported that ion exchange was occurring with the H^+ ion from water.(15,17,20,28) However, recent findings indicate that a more complex water species is involved, such as H_3O^+.(27,72)

The removal of alkali ions from glass by aqueous solutions is several orders of magnitude more rapid than can be accounted for by their diffusion rates in the bulk unreacted glass. This has led some researchers to question the theory of a diffusion-controlled process because of an initial square root of time dependence.(30,40,73) Measurements of both the sodium diffusion coefficients and sodium leach rates on a series of simple silicate glasses have been made.(40) There was no correlation found between diffusion coefficients and leach rates.

At least one calculation exists in the literature which attempts to explain the apparent enhanced diffusion observed for alkali ions in glass when exposed to aqueous solutions.(73) The enhanced diffusion can be accounted for by a negative charge which develops on the glass surface as a result of initial reactions with the hydroxyl groups in the water. This surface charge then accelerates alkali ion diffusion in the near-surface region. A surface charge of approximately 200 millivolts is necessary to sufficiently enhance alkali ion diffusion. A surface charge of approximately this magnitude has been reported for a simple silicate glass.(74)

As a result of the previous discussions of important effects on glass leaching, it can be concluded that a predictive model to be used for elemental release from a waste form under repository conditions must incorporate many effects. These effects include pH, temperature, leachate composition, radiolysis, solubility limits, and flow rates. Modeling of the glass-water interaction is, therefore, a difficult task.

Several models have been proposed to describe glass leaching in aqueous solutions.(15,17,18,27,28) Only a brief description will be presented here. However, a more thorough review is given elsewhere.(30) These models are all primarily applicable to relatively simple glasses containing only a few elements compared to the many in typical waste containment glasses. Most of the models are similar in nature with varying degrees of sophistication. Essentially all of the models involve solid state diffusion and predict a square root of time dependence for initial leaching, suggesting a diffusion-controlled process, and a linear time dependence for longer leaching times, indicating corrosion or congruent dissolution.

Two of the models warrant mention because of special features. The model of Doremus(27) incorporates the interdiffusion of alkali ions with hydronium ions in the water, and the model by Hench(17) incorporates pH.

Waste glass-water interactions are complex, and the models presently utilized to explain these interactions have been adapted from the results of simpler silicate glasses. These results were normally obtained under limited conditions with no intent to simulate or investigate behavior in a repository. Realistic predictive models for waste-glass leaching under repository conditions should incorporate the phenomena that are occurring during the glass-water interaction. The controlling parameters must be identified and characterized so that mathematical descriptions can be developed for them. As described in the previous sections, the controlling parameters have been identified and quantified to varying degrees. These parameters are pH and Eh effects, temperature effects, leachate composition effects, radiation effects, solubility effects, and leachate flow effects. Enough information currently exists to quantify all of the controlling parameters reasonably well.

Currently, realistic models for borosilicate waste glass leaching characteristics are being developed, incorporating the state of knowledge of the previously described effects, but significant results have not as yet been published. These realistic models will be the base from which alterations or interactions caused by other repository constituents can be determined.

3.2 SPENT FUEL

Spent fuel is inherently a simpler material than borosilicate waste glass. However, the properties of irradiated fuel are dependent upon the irradiation history. As a result, irradiated fuel is not a single product but a range of products whose overall chemistry is dominated by the chemistry of UO_2.

The chemistry of UO_2 fuel is dependent on such parameters as the O/U ratio, the extent of burnup, and the power rating.(75) The physical changes which occur during irradiation include grain growth, fuel cracking, and the production of both closed and open porosity due to the formation of fission gas bubbles at grain boundaries. Chemical and physical factors combine to produce a high surface area material which is inhomogeneous on both the micro- and macroscale. This inhomogeneity is reflected to a considerable extent in the results which have been reported for spent fuel leach tests.

Unlike glass, the majority of spent fuel leaching investigations have been conducted recently.(76-81) Since spent fuel is highly radioactive, leaching experiments must be performed in a hot cell. Therefore, the number of facilities available for this type of work and the expense have limited the investigations to a few locations. Additionally, relatively few surface analyses can be performed on such a highly radioactive material, which hinders understanding.

A summary of most of the spent fuel leaching investigations is given in Table 3-3. The three laboratories represented are Battelle Pacific Northwest Laboratories (PNL), Los Alamos Scientific Laboratory (LASL), and Whiteshell Nuclear Research Establishment (WNRE). The spent fuel source, burnup, experimental descriptions including leachate type, sample configuration, and time span of the experiments are also given. As can be seen, many long-term tests have been conducted, and the sample configurations vary from chunks of spent fuel which have been removed from the cladding to segments of fuel which have the cladding intact.

TABLE 3-3. Leach Test Parameters on Spent Fuel.

Laboratory	Reactor	BU (GWD/MTU)	Experiment Description	Conditions of Fuels	Time Span
PNL	Quad City BWR H. B. Robinson PWR Zorita PWR	9 28 54	25 C Paige Test Hanford Ground Water Synthetic Sea Water Deionized Water	Chunks	Up to 1400 days D.I. water; up to 822 days for other
PNL	H. B. Robinson	28	M - IAEA - 25 C Deionized Water WIPP "B" Brine 0.015 M $CaCl_2$ 0.03 M $NaHCO_3$ 0.03 M NaCl	Chunks	Up to 769 days
PNL	H. B. Robinson	28	Static - 25 and 75 C Only 25 C completed All 5 solutions listed above	Chunks	Up to 340 days
			Static 150 and 250 C Deionized Water 0.03 M $NaHCO_3$ WIPP "B" Brine		Under way
LASL	H. B. Robinson	28	IAEA - 25 and 70 C Reducing and oxidizing Deionized Water	Clad	Up to 78 days
WNRE	Pickering-Candu	7.9	Static - 25 and 150 C Granite Ground water Carbonate Ground water Reducing and oxidizing conditions	Clad	Up to ∼500 days

Irradiated fuel experiences large temperature gradients from its axial center to the cladding. This results in a range of porosity, grain size, and elemental variations from the center to the edge of spent fuel.(75,76) For example, ^{137}Cs concentrates at the fuel-cladding interface. Since spent fuel is highly cracked, removal of the cladding results in small chunks of fuel with wide size and property distribution. Investigators therefore have a choice of spent fuel chunks or a segment of spent fuel with the cladding intact for leaching samples.

If fuel segments including cladding are used, the entire range of spent fuel is exposed to the leachate. This hopefully allows the average leaching characteristics to be determined. However, because of the extensive cracking and fuel-cladding interface, the surface area exposed to the leachate is not known and can vary from sample to sample. Furthermore, relatively large amounts of ^{137}Cs are concentrated at the fuel cladding interface which is preferentially leached. Therefore, leaching from the spent fuel alone is not being measured. Rather, the combination of spent fuel and fuel-cladding interfacial leaching is being determined. Additionally, the cladding can act as a sorptive surface for ions which have been removed from the sample. Thus, leaching results are difficult to interpret using this sample type.

If spent fuel chunks without the cladding are used, leaching results are only for the spent fuel and do not include fuel-cladding interfacial leaching or sorptive effects of the cladding. Additionally, a reasonable measure of surface area exposed to the leachate can be made. However, the chunks are very inhomogeneous and, unless large numbers of them are used as a sample, representative spent fuel leaching results will not be obtained, and sample-to-sample variations can be large.

There is no one best representative spent fuel sample type. Each one has its shortcomings. Since each investigator has used dissimilar leaching samples and experiments, it is not possible to directly compare results. However, general observations are that leaching is initially incongruent, with ^{137}Cs and ^{90}Sr being leached more rapidly from the fuel in the short term. At longer times congruent leaching is approached. Most researchers have incorporated UO_2 into their leaching programs as an aid to understanding the more complex and difficult to work with spent fuel. The following discussions will attempt to describe what has been learned about some of the important effects on spent fuel leaching.

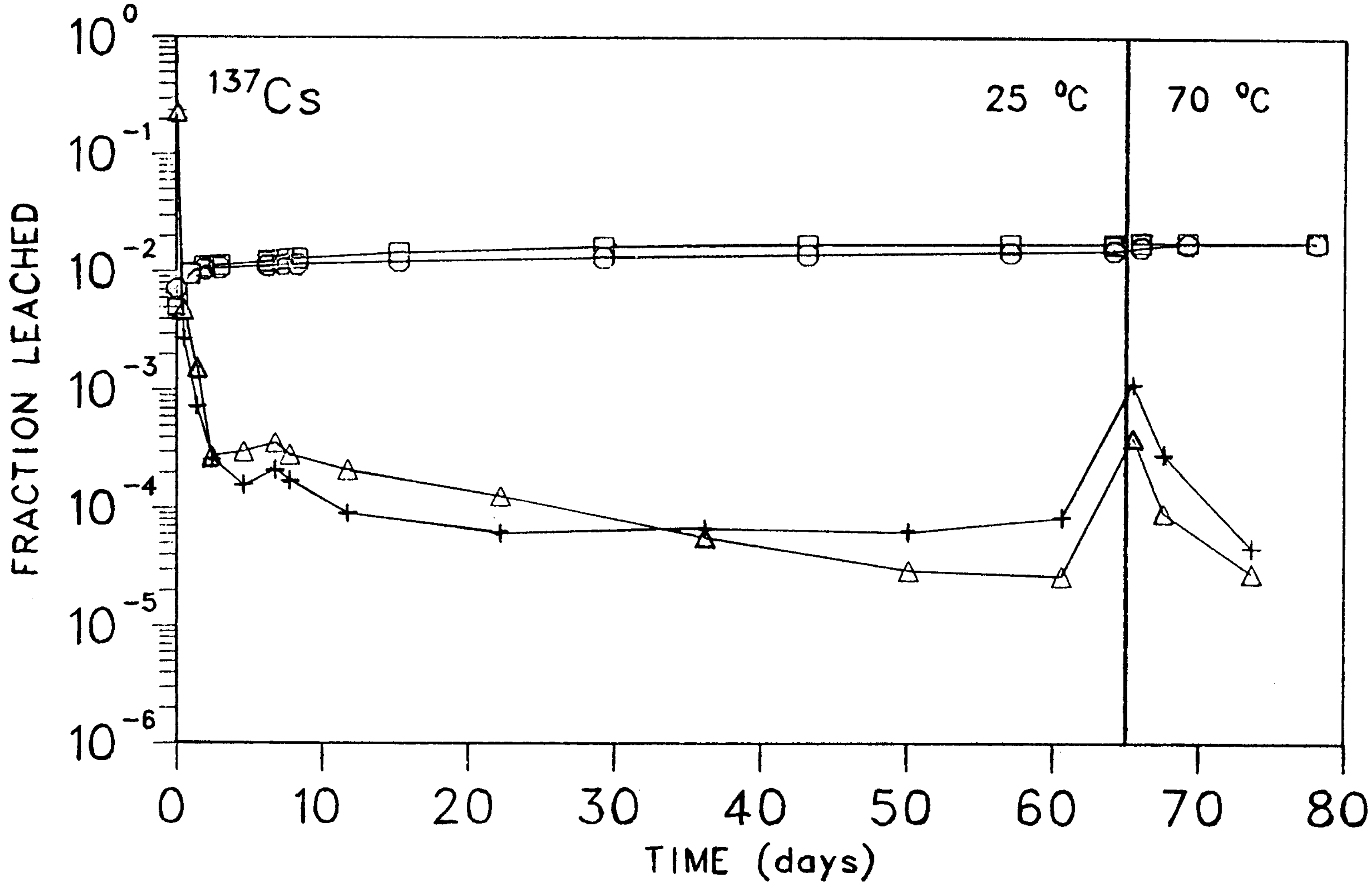


FIGURE 3-9. Effects of Temperature on Leaching of ^{137}Cs from Spent Fuel Where □ and ○ Are Cumulative Fraction Released Under Reducing and Oxidizing Conditions, Respectively, and Δ and + Are Leach Rates in Reducing and Oxidizing Conditions, Respectively. (Ref. 77)

3.2.1 Temperature Effects

As can be seen from Table 3, only a small amount of temperature effect data is available. There are, however, experiments in progress which will significantly add to this data bank when completed and reported.

The temperature effects on spent fuel leaching are very small. Differences in leaching characteristics in demineralized water have been measured at 25 and 70 C at LASL(77) and at 25 and 150 C at WNRE.(76) An example of these results is shown in Figure 3-9 for ^{137}Cs. As can be seen, the ^{137}Cs leach rate initially increased with a temperature increase from 25 to 70 C, then rapidly decreased again to essentially the original value. The rapid fluctuation in leach rate did not noticeably affect the cumulative fraction ^{137}Cs removed from the sample. For most of the other ions leached from spent fuel, increasing the temperature from 25 to 70 C caused a decrease in the leach rate and in the cumulative fraction leached. Nearly identical results have been reported for temperature increases from 25 to 150 C.(76) Increases in temperature normally resulted in enhanced plateout of elements on container walls but only minor elemental changes in the leachate. The lower leach rates for most elements at enhanced temperatures may be related to a number of factors, including oxide film growth or a lower U(VI) oxide solubility at higher temperatures.(82)

3.2.2 Oxygen Level Effects

The effects of oxygen on leaching of spent fuel are expected to be significant.(76,83) Here again, only limited data are available for consideration.(76,77) The work conducted at WNRE utilized 25 C distilled water at three oxygen partial pressures obtained with gaseous mixtures and a platinum gauze catalyst. The oxygen concentrations are 2.5×10^{-4}, 6.1×10^{-6}, and 1×10^{-6} mole $\cdot$ kg^{-1}. Oxidizing and reducing conditions were also utilized for spent fuel leaching in deionized water at 25 C by LASL. Again, these oxygen levels were obtained by use of gaseous mixtures and had Eh values of +0.55 V for the oxidizing solution and -0.12 V for the reducing solution. Both laboratories found essentially the same results. ^{137}Cs leach rates are independent of oxygen concentration (see Figure 3-9 as an example), verifying that the initial release of cesium is from leachable phases and that matrix breakdown is not required for this to occur. In general, dissolution rates for the other elements are decreased with decreasing oxygen in the leachate, but not to the extent which would be expected if a first-order dependency of rate on oxygen concentration were to be obeyed.(83) This could possibly be attributed to the oxidation of the fuel surface during sample preparation. Once the surface is partially oxidized the dissolution process may become more facile, and the rate becomes somewhat insensitive to changes in oxygen concentration. An example of the effect of oxygen on leach rates of elements removed from spent fuel is given in Figure 3-10 for $^{239+240}Pu$.

3.2.3 Leachate Composition Effects

Spent fuel leaching experiments have been conducted in simulated ground waters by several researchers.(76,78-81) The results are partially conflicting and difficult to explain. Findings from WNRE(76) after leaching in deionized, granite, and carbonate ground waters are that leach rates of ^{90}Sr, $^{239+240}Pu$, and rare earths are generally somewhat lower in ground waters than in air-saturated distilled water. Uranium, the exception, had a leach rate of more than an order of magnitude higher in both simulated carbonate and granite ground waters compared to distilled water. This was presumably due to carbonate complexing. Eklund and Forsyth(78) from KBS in Sweden used distilled water and the identical carbonate ground water as WNRE in their spent fuel leaching experiments and found that the final dissolution rate for uranium was the same for both leachants.

PNL has used deionized water and four other generic ground waters as leachates for spent fuel leaching tests.(80,81) The generic ground waters are 0.03 $\underline{M}$ $NaHCO_3$, WIPP "B" saturated salt brine, 0.03 $\underline{M}$ NaCl, and 0.015 $\underline{M}$ $CaCl_2$. Results were that essentially all elements leached more rapidly in air-saturated deionized water (including uranium) than in any of the air-saturated ground waters. These results are in agreement with WNRE except for uranium. PNL found uranium to leach in excess of an order of magnitude faster in deionized water than in the generic carbonate ground water, with less difference observed for other ground waters. Obviously, carbonate complexation cannot be used to explain these results.

There are three different experiments comparing ground waters to deionized water leaching results from spent fuel. The results are consistent for most elements, that is, ground waters reduce leach rate. However, there is total disagreement for uranium. More experiments need to be conducted to resolve this discrepancy.

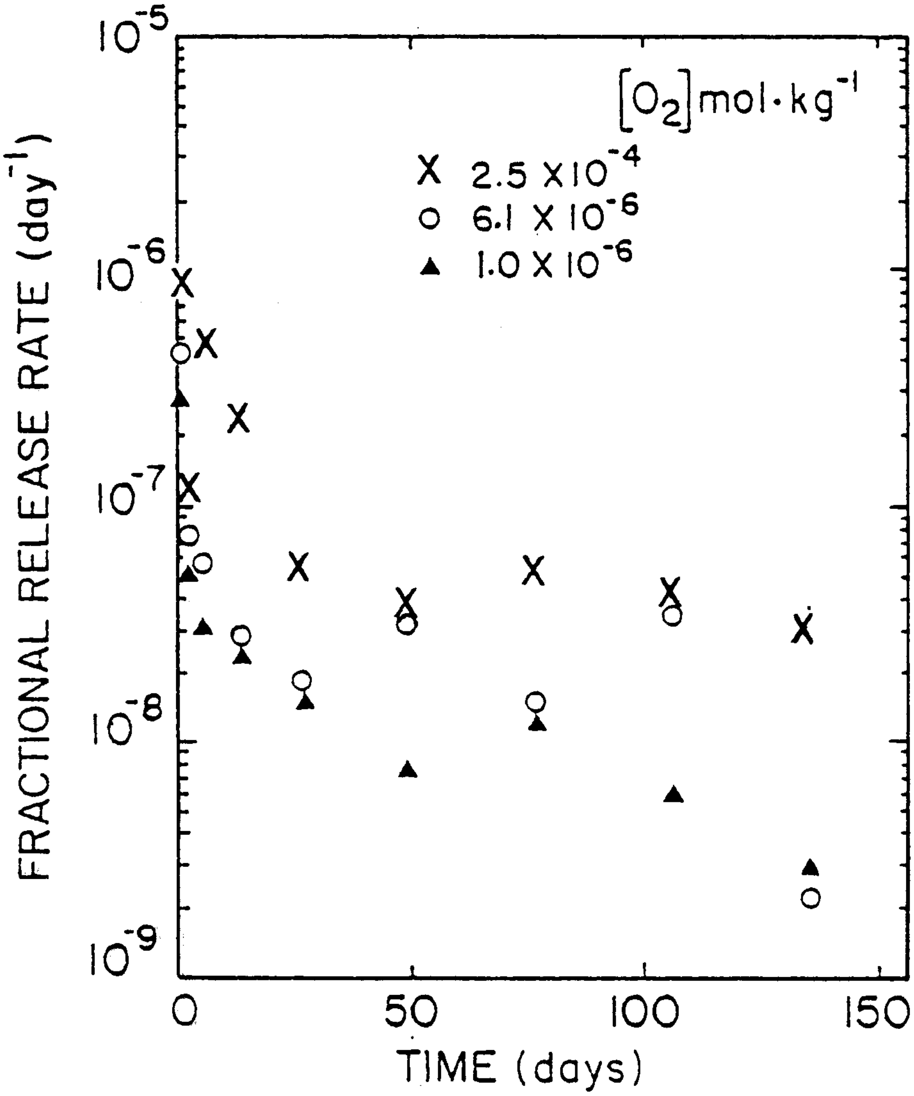


FIGURE 3-10. Fractional Release Rates of $^{239+240}Pu$ from Spent Fuel at Various Oxygen Concentrations at 25 C. (Ref. 76)

3.2.4 Solubility Effects

Solubilities have not been investigated to any extent for spent fuel. However, several solubility studies have been conducted on UO_2.(84-86) UO_2 is so insoluble in neutral and alkaline solutions under reducing conditions that measurement of its equilibrium solubility presents difficulties in analysis.(76) Under very reducing conditions, dissolution of UO_2 involves only the U(IV) valence state. The low solubility of UO_2 observed in slightly acidic and alkaline water increases sharply under even mildly oxidizing conditions because of the formation of the U(VI) species,

UO_2^{+2}, and its hydrolysis products.(76) Many ground-water species complex with UO_2^{+2}, thereby increasing the UO_2 solubility. UO_2 or spent fuel solubilities in ground waters have not been adequately investigated. A more thorough review of UO_2 solubility results is given elsewhere.(76,84-86)

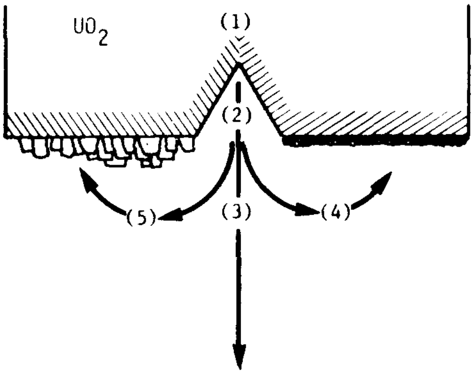
3.2.5 Mechanisms and Models

Similar mechanisms for the interactions of UO_2 with aqueous solutions have been proposed by at least two different sources.(76,87) In neutral or reducing conditions, dissolution of UO_2 involves only the U(IV) valence state, and the equilibrium solubility is very low. However in solutions containing oxygen or oxidizing species, many reactions can occur depending upon temperature and pH. These reactions have been summarized by Wang(87) and are illustrated in Figure 3-11. Implied in this model is the fact that even after the solubility limits have been reached, dissolution can still occur as long as precipitation is also occurring. If this applies to spent fuel, then elemental removal does not stop when the solubility limit for UO_2 has been reached. Rather, dissolution and precipitation can continue to occur, which would release other elements whose solubility limits may not have been reached.

Spent fuel contains grain boundaries, large inhomogeneities, and radiation damage. Therefore, it is not clear whether spent fuel will react with aqueous solutions in a manner similar to UO_2. The leaching mechanisms of spent fuel may be more complex and require direct evaluation.

3.3 COMPARISONS OF GLASS AND SPENT FUEL LEACHING

In general, spent fuel releases elements to aqueous solutions at a faster rate than borosilicate waste glass. This is illustrated in Figure 3-12 for some elements common to both waste forms. The leachate was deionized water, and the leaching results were normalized by the weight fraction of the element in the sample. As can be seen, there is a difference of nearly two orders of magnitude in leach rates. These results represent the largest difference. If sodium bicarbonate leachate is used, the results are quite different (Figure 3-13). With this leachate, borosilicate glass and spent fuel have similar leach rates after a few days. This represents the other extreme. Other generic ground waters fall somewhere between deionized water and sodium bicarbonate solution. These solutions were all air-saturated, and therefore different results might occur for the same solutions under reducing conditions.



REACTIONS

(1) SURFACE OXIDATION (several angstroms)

$UO_2 + x/2\ O_2 \longrightarrow UO_{2+x}$, $\qquad 0 \le x \le 1$

(2) OXIDATION-DISSOLUTION

$UO_{2+x} + 2H^+ + (1-x)/2\ O_2 \longrightarrow UO_2^{+2} + H_2O$, $\qquad pH < 4$

$UO_{2+x} + H^+ + (1-x)/2\ O_2 \longrightarrow UO_2(OH)^+$, $\qquad 4 \le pH \le 7$

$UO_{2+x} + H_2O + (1-x)/2\ O_2 \longrightarrow UO_2(OH)_2^0$ $\qquad pH \ge 7$

(3) TRANSPORT

(4) HYDROLYSIS--FILM FORMATION, 25 to 75°C

$UO_2^{+2} + 3H_2O \rightleftharpoons UO_3 \cdot 2H_2O + 2H^+$, $\qquad pH \le 4$

$UO_2(OH)^+ + 2H_2O \rightleftharpoons UO_3 \cdot 2H_2O + H^+$, $\qquad 4 \le pH \le 7$

$UO_2(OH)_2^0 + H_2O \rightleftharpoons UO_3 \cdot 2H_2O$, $\qquad pH \ge 7$

(5) HYDROLYSIS--CRYSTAL GROWTH, 150°C

$UO_2^{+2} + 2H_2O \rightleftharpoons UO_2(OH)_2 + 2H^+$, $\qquad pH \le 4$

$UO_2(OH)^+ + H_2O \rightleftharpoons UO_2(OH)_2 + H^+$, $\qquad 4 \le pH \le 7$

$UO_2(OH)_2^0 \rightleftharpoons UO_2(OH)_2$, $\qquad pH \ge 7$

FIGURE 3-11. Oxidation and Dissolution Mechanisms for UO_2 in Deionized Water. (Ref. 87)

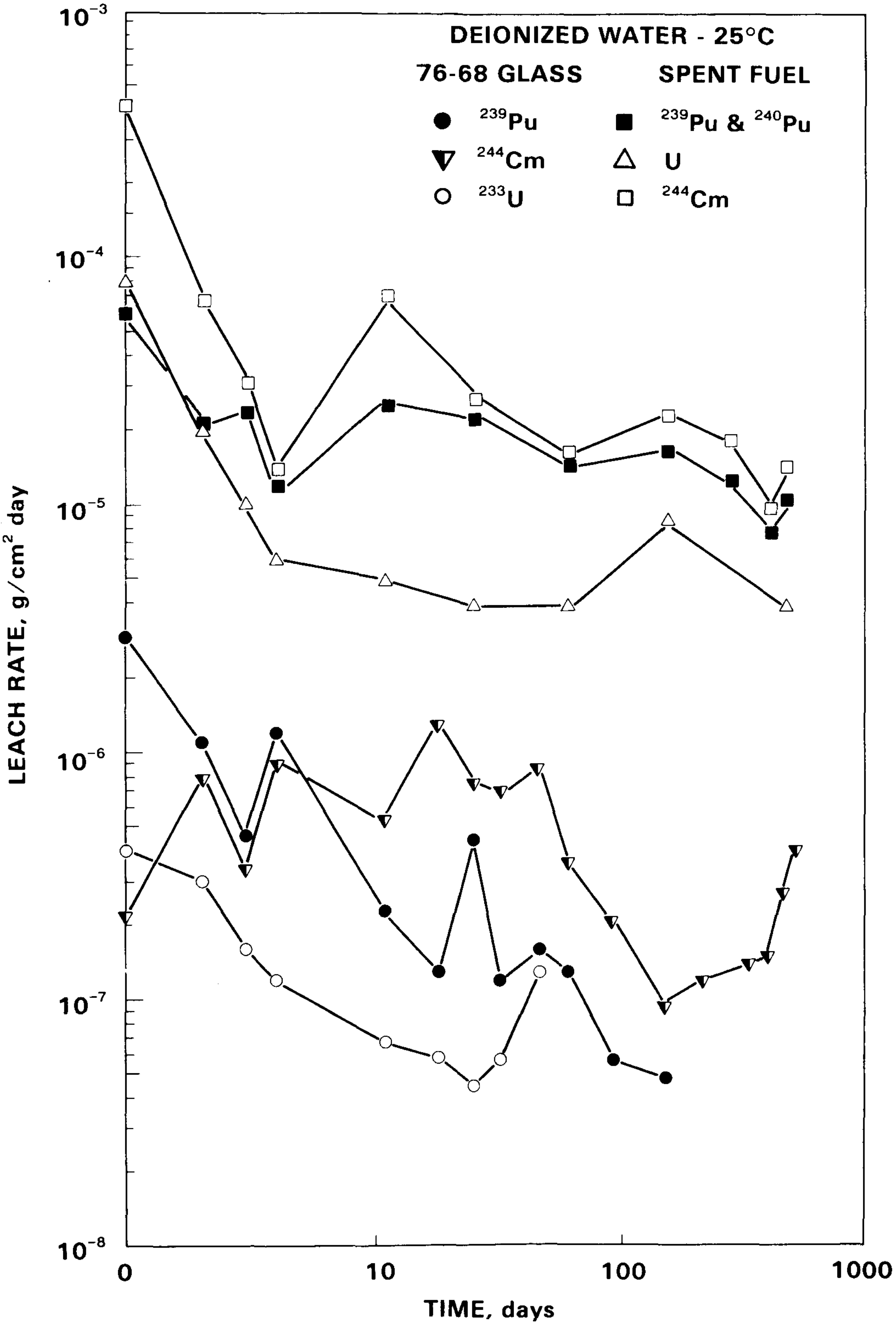


FIGURE 3-12. Comparison of Elemental Leach Rates from Spent Fuel and PNL 76-68 Glass in Demineralized Water at 25 C.

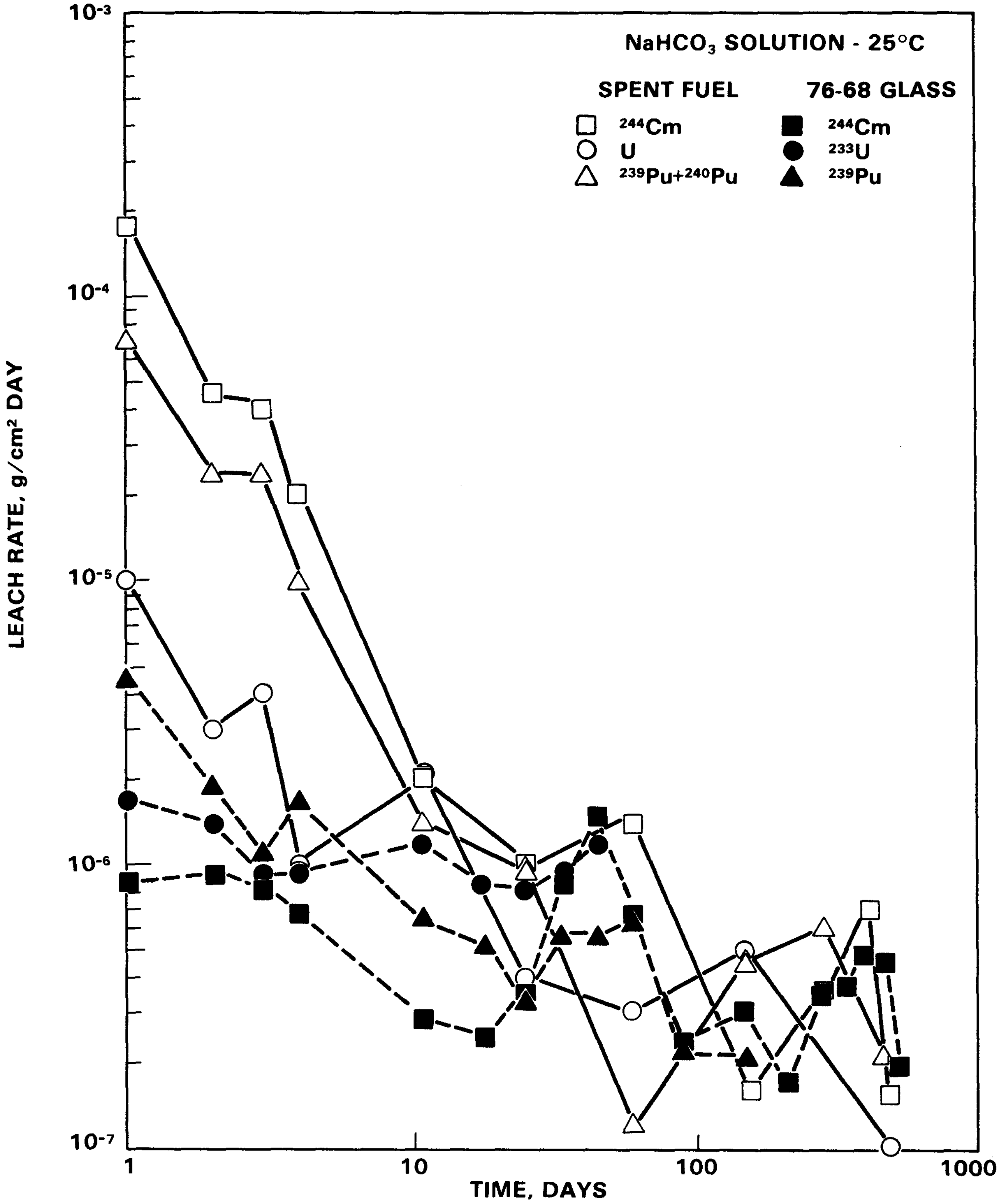


FIGURE 3-13. Comparison of Elemental Leach Rates from Spent Fuel and PNL 76-68 Glass in 0.03 M $NaHCO_3$ Solution at 25 C.

4 CONCLUSIONS

A large body of information on the interactions of glass and spent fuel with aqueous solutions has been reviewed, compared, and discussed. The following conclusions can be made:

- There is a fundamental difference in the pH dependence of leaching for simple silicate and borosilicate waste glasses. The waste glasses are more durable in the basic pH range, while the silicate glasses are more durable in the acidic pH range.
- Temperature dependencies for elemental leaching from borosilicate waste glasses have activation energies ranging from 7 to 22 kcal/mole and typically have linear log leach rate versus reciprocal temperature dependencies over wide temperature ranges.
- Elemental leach rates from spent fuel have essentially no temperature dependency over the temperature range of 25 to 150 C. This conclusion is based on leachate concentrations alone and does not consider plateout on container walls.
- The variation in elemental leach rates from borosilicate glass between deionized water and for simulated ground waters is one order of magnitude or less. The simulated carbonate ground water typically results in the highest leach rates.
- The elemental leach rates from spent fuel are less in simulated ground waters than in deionized water. The possible exception to this is the uranium leach rate for which a large discrepancy exists in the literature.
- Lowering the oxygen content of the leachate decreases the leach rates of most elements in spent fuel. The notable exception is cesium, which is insensitive to the oxygen content of the leachate.
- Radiation damage in borosilicate waste glasses occurs because of the radioactive waste contained in the glasses. The most damage is caused by alpha decay, primarily from the recoil nucleus. This damage, caused by self-radiation, results in only minor changes in the leaching characteristics of the glass.
- Radiolysis of the leachate results in enhanced leaching of borosilicate waste glasses. The enhancement is largest at lower temperatures

and diminishes with increasing temperature. If nitrogen is present in the leachate, nitric acid is formed as a result of radiolysis. This greatly enhances leaching at all temperatures.

- The solubility limits of plutonium and neptunium from borosilicate waste glasses are identical to those found for PuO_2 and NpO_2, indicating that these oxides may be controlling the solubility in the glass.
- Elemental release from spent fuel is typically higher than from borosilicate waste glasses. The only exception to this is in simulated sodium bicarbonate ground water, where their rates are nearly the same.
- Models for both spent fuel and borosilicate glass leaching are currently not adequate to reliably predict long-term leaching characteristics. However, the new generation of models presently being developed should be adequate for predictive purposes.
- The effect of flow rate of the leachate on elemental release is not large for reasonable simulated ground-water flow. The effect is somewhat temperature-dependent, with a larger effect occurring at higher temperatures.

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