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DEC 03 1982

WMHL: 3101.1

WM Record File  
1011

WM Project WM-10  
Docket No. \_\_\_\_\_

MEMORANDUM FOR: John B. Martin, Director  
Division of Waste Management

PDR   
LPDR

FROM: Michael J. Bell, Chief  
High-Level Waste Licensing  
Management Branch  
Division of Waste Management

Distribution: \_\_\_\_\_  
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(Return to WM, 623-SS)

SUBJECT: OPS PLAN COMMITMENTS

Attached are the draft Appendices D, P, Q and R and draft Site Issue Analyses in the areas of Waste Package, the Site Selection Process and Environmental Factors of the Site Characterization Analysis, due today, December 3, 1982. This completes OPS Plan Commitments #311221C and #311221D which are assigned to this branch.

Original Signed by  
MICHAEL J. BELL  
Michael J. Bell, Chief  
High-Level Waste Licensing  
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Enclosures:  
As stated

cc: R. J. Wright, WMHT

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SYSTEMS ANALYSIS OF A HLW REPOSITORY AT HANFORD, WASHINGTON

DRAFT SITE CHARACTERIZATION ANALYSIS - APPENDIX D

I. INTRODUCTION

This section discusses the reasons for performing a systems analysis of the proposed Hanford repository at this time, and briefly describes the components of such an analysis. Section II briefly discusses the functions which a repository must perform to protect public health and safety and describes both the engineered and geologic features of a repository which must be considered in evaluating those functions. Section III describes an assumed environmental standard for the allowable releases from a HLW repository and a simple model which relates this standard to the expected performance of the Hanford repository. Section III also includes a description of the data used in exercising the model and a discussion of that data. Section IV discusses the results of this model for the routine long term performance of the repository. Section V contains an analysis of the impact of failed borehole and shaft seals on the performance of the repository.

This report is an initial assessment of the performance of the Hanford repository, based on information now available. It is intended to assess the effects of uncertainties on the likelihood that the repository will be able to comply with the draft EPA Standard, 40 CFR 190, and the 1,000 year groundwater travel time performance objective of the draft NRC technical rule, 10 CFR 60. It also identifies the major variables which are likely to be important in demonstrating compliance with these regulatory products at the Hanford site to better guide the NRC evaluation of the adequacy of DOE's site characterization plans. These variables are identified based on current estimates of the ranges and distributions of their values based on information available in the SCR. The report also assesses the impact of containment time and release rate on the performance of the overall repository, and the effect of these variables on the

performances which will be required of individual components of the geologic system in order to reach compliance with the draft EPA standard.

The analysis reported here requires three components; a figure of merit, which is the benchmark against which the performance of the repository is judged, a model which relates the variables likely to affect system performance to the figure of merit, and the data which consists of the values which the variables can reasonably be expected to take. In this case there are two figures of merit; the draft EPA standard and the 1,000 year groundwater travel time performance objective. The model is a simplistic quasi-two dimensional Darcy flow description of the Hanford Site which is exercised using the computer codes NWFT/DVM and EZHANF, and the data base consists of best estimates of the ranges and distributions of pertinent flow and transport properties at the Hanford Site available in the published literature, with emphasis on the values contained in the SCR.

## II. DESCRIPTION OF A GEOLOGIC REPOSITORY

The primary function of a mined geologic repository is to isolate the waste so that only small quantities of the wastes would return to the environment over such long times that disposal would not constitute an unreasonable risk to public health and safety. The principal mechanism by which radioactive material is anticipated to be released to the environment from a geologic repository is by contamination of groundwater (Ref. 3-2) that contacts the emplaced waste and transports the radioactive materials from the repository to locations in the environment where they can be ingested or contacted by humans. Thus, the assessment of how well a repository performs its isolation function involves consideration of the time when groundwater initially contacts the waste, the rates at which groundwater can contact the waste, the quantities and concentrations of radioactive materials which may be transported away from the disposal facility, and the rates of transport of the radionuclides through the geologic, hydrologic and geochemical systems to the accessible environment.

In order to emplace the wastes, the repository must be open for a period of years during which wastes would be received and handled in surface facilities,

transported to the underground facility and placed in disposal locations. After this period of operation, the repository would be sealed and permanently closed. Until the time of permanent closure, handling of the radioactive materials would be carried out so that the public and workers would be protected from excessive exposure to radiation. The measures taken to protect the public and workers during the pre-closure period would be similar to those taken for radiation protection at other nuclear facilities and are not discussed further.

In light of the hazards of the radioactive materials in the HLW and the long times involved, the measures required to achieve successful isolation of HLW are unique. There are substantial uncertainties involved in such factors as the release rate of wastes from a repository, pathways by which the wastes might reach the environment, and the physical and chemical conditions likely to reflect the travel times of wastes along these pathways. These uncertainties will be discussed in more detail in Section III.

#### Description of a Geologic Repository

A mined geologic repository is a facility which achieves isolation (limiting the rate of waste release to the accessible environment to acceptable levels) by means of two major subsystems. These are the geologic setting itself, which is selected for geologic, hydrologic and geochemical attributes which can contribute to isolation; and the engineered system consisting principally of waste packages and materials used to backfill and seal the underground facility, boreholes and shafts. The geologic setting and the engineered system differ both in their contributions to isolation and in the degree of confidence which can be placed on predictions of their long-term performance. Any mined geologic repository will contain some combination of these engineered and natural barriers which together must provide isolation. This is commonly called the multiple-barrier or the defense-in-depth approach.

## Engineered Barrier System

The engineered barrier system can contribute to isolation first by controlling the release rate of radioactive materials to the geologic setting, thereby reducing the contribution which the geologic setting must make, and second, by providing a source of isolation which is relatively independent of the geologic setting and which can therefore mitigate the consequences of unforeseen failure of that setting. This control of the source term can be achieved in several ways. First, the engineered barrier system can be designed of materials that limit the rate at which groundwater can contact the wastes. Second, the waste form itself can be comprised of, or encapsulated in, leach resistant materials. Third, materials which can retard migration once leaching has occurred can be placed in the underground facility and around the canisters to further control release of radioactive materials to the geologic setting.

## Geologic Setting

Following release of the radioactive materials from the engineered barrier system, the geologic setting alone must provide whatever additional isolation is needed to keep radioactive materials entering the accessible environment to acceptable levels. The geologic setting can provide the needed isolation by two principal means. First, the geologic setting can exhibit hydrologic conditions which result in low groundwater velocities and long groundwater travel times to the accessible environment. Second, the geologic setting can be comprised of materials that chemically inhibit transport of radionuclides by groundwater by, for example, ion-exchange or precipitation reactions. The objective is for the geologic setting, through long groundwater travel times and geochemical retardation, to delay the arrival time of radionuclides at the accessible environment for many thousands of years. During this time additional radioactive decay will take place, so that only a small fraction of the material released from the engineered barrier system will enter the accessible environment, and then only very far in the future.

### III. SYSTEM MODEL OF THE HANFORD REPOSITORY

Draft 19 of the EPA standard has been employed to show the relationship between overall system performance and the numerical requirements on the engineered barrier system and the geologic setting. This draft fixes a number of parameters against which the overall performance of a repository will be evaluated, including a location at which performance is to be measured (the boundary of the accessible environment), a measure of performance (cumulative releases of specific radionuclides measured in curies), and an interval during which performance is to be measured (10,000 years). Specific limits for releases for reasonably foreseeable (anticipated) processes and events appear in Table 1, and were applied here in accordance with the footnote to that table. For purposes of our assessment, consistent with the assumed standard, the accessible environment is assumed to be all areas on the land surface regardless of distance from the repository and to include all subsurface locations beyond a vertical surface 10 km away from the location of the emplaced wastes. These boundaries appear in Figure 1.

The following nuclides were included in these analyses:

Retarded fission products: Sr-90<sup>\*</sup>, Cs-135<sup>\*</sup>, Cs-137<sup>\*</sup>, Sn-126<sup>\*</sup>,

Unretarded fission products: C-14<sup>\*</sup>, Tc-99<sup>\*</sup>, I-129

Activation products: Ni-59, Zr-93

Actinides: Am-243<sup>\*</sup>, Am-241<sup>\*</sup>, Pu-241, Pu-240<sup>\*</sup>, Pu-239<sup>\*</sup>, Np-237<sup>\*</sup>,  
U-234

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\* Releases of these nuclides are specifically limited by the working draft EPA standard.

These nuclides were included for the following reasons:

- ° All the nuclides specified in the working draft EPA standard were included with two exceptions (Pu-238 and Ra-226).
- ° The half-life of Pu-238 is sufficiently short that releases via groundwater would not contribute significantly to the total amount of plutonium released.
- ° The inventory of Ra-226 does not build up sufficiently within the first 10,000 years to allow this nuclide to contribute significantly.
- ° I-129 was included because of its unique combination of chemical and biological characteristics and a very long half-life.
- ° Ni-59 and Zr-93 may be present in spent fuel in moderate quantities and, because of long half-lives, could contribute to releases.
- ° While Pu-241 is not named in the EPA standard, it was included in these analyses because it is a parent of Np-237.
- ° U-234 is the most abundant uranium isotope present in spent fuel (in terms of radioactivity), and therefore provides the best estimate of the releases to be expected for uranium.

#### Routine Release Scenario: The Undisturbed Repository

It is anticipated that if radionuclides are released from an undisturbed repository to the accessible environment, this release will take place by failure of the container surrounding the wastes, dissolution of the wastes by groundwater, and migration of the radioactive material dissolved from the wastes with the groundwater to the accessible environment. A diagram of this scenario appears in Figure 1. In this scenario, groundwater is presumed to resaturate the repository within a few centuries after closure and to initiate deterioration of the waste packages, causing eventual breaching of the waste

packages and start of radionuclide release to the underground facility. In time, the radionuclides are released to the geologic setting. The assumption of prompt resaturation is conservative but reasonable because void spaces in the backfilled repository will result in a hydraulic gradient that will tend to promote flow inward, and because some natural leakage is anticipated. An upward hydraulic gradient in the geologic setting is assumed, causing groundwater carrying the radionuclides to move vertically through the host rock from the repository to an overlying aquifer. The radionuclides then follow the groundwater flowpath horizontally along the Frenchman Springs member away from the repository and eventually reach the accessible environment. Transport of some radionuclides through both the host rock and the aquifer is assumed to be impeded by chemical retardation and by limitations on radionuclide solubility. Alternative release paths might be selected, such as a downward gradient which could move radionuclides to an underlying aquifer. However, thermal effects will tend to enhance transport to an overlying aquifer, so this upward case is considered reasonable. Evaluation of this scenario involves prediction of the behavior of an undisturbed repository taking into account uncertainties associated with significant parameters.

#### Numerical Assessment: The Model Chosen

To quantify the effects of numerical requirements for the engineered barrier system and the geologic setting in the routine release scenario, it is necessary to specify a quantitative model which corresponds to the qualitative description above. That model may then be used to determine how each of the barriers affects the performance of the overall geologic repository. The model selected for describing this scenario is a quasi-two dimensional model in which the radionuclides travel vertically upward, both through the underground facility from it to the aquifer, after which they travel horizontally along the aquifer. This model approximates the groundwater flow shown in Figure 1 by a series of legs, shown in Figure 2. Legs A and B correspond to the Frenchman Springs Member, leg C corresponds to flow through the underground facility itself, and leg D corresponds to flow from the underground facility through the overlying basalt flows and interbeds separating the underground facility from the Frenchman Springs Member.

A number of simplifying assumptions have been made in order to implement this model. These assumptions are consistent with generally accepted practice in transport modeling and are not intended to introduce either conservatism or non-conservatism into the analysis. First, one-dimensional Darcy flow is assumed, implying low Reynolds number flow in porous media, and implying that all significant flow is unidirectional. Low Reynolds number flow is reasonable in view of the small conductivities and hydraulic gradients involved in geologic disposal systems. Porous flow is reasonable for the Frenchman Springs Member. But for the vertical flow from the underground facility to the Frenchman Springs Member, flow through fractures is likely. Therefore, the hydraulic conductivity has been adjusted for leg D to roughly approximate fracture flow. Presumption of unidirectional flow in the legs has been shown to lead to good agreement with complex multi-dimensional models such as SWIFT (Ref. 7-1) for applications similar to this one (Ref. 7-2 and 7-3).

The model also presumes that rock properties are invariant for the length of an individual leg, so that properties such as permeability and chemical retardation are constants. A radionuclide passing through an actual unit is likely to encounter a spatially varying environment that may affect its velocity. The constant properties of the leg specified in the model therefore are spatial averages of estimates of the aquifer properties, so that a radionuclide is modeled to traverse the leg in the same length of time it would take to traverse the aquifer unit the leg represents. Further, the ranges of the properties considered below are considered to encompass the changes in these properties that are anticipated to occur along actual aquifer units.

Another simplification made by this model is that it does not account for all of the effects of the heat released by the waste. The model does account for thermal buoyancy effects on flow in leg D, by adjusting the pressure at point 2, the point where flow enters the underground facility. The model does not account, however, for possible permeability changes in the overlying host rock which might result from thermomechanical effects. Finally, as applied here, the model does not deal with the specific processes which cause canister failure or which affect radionuclide release rates from the engineered barrier system. It therefore does not deal with the uncertainties associated with early failure of

containment such as hydrothermal dissolution of waste forms or failure of the backfill to retard radionuclides due to elevated temperatures or radiation fluxes.

Clearly, the model described above is highly idealized, and the behavior and models of an actual site will probably be much more complex. However, it is the staff's view that the model is more than sufficient to accomplish its purpose in this document. That is, the model provides significant, realistic insight into the relationship between major variables and repository performance.

To implement this model, the NWFT/DVM code was used (Ref. 7-4 and 7-5), which requires an extensive set of parameters as input data. These parameters, whose selection reflects the assumptions mentioned above, have been divided into two groups; the first is subject to relatively little uncertainty, the second reflects many of the sources of uncertainty inherent in modeling hydrologic flow and transport. The first, to be called fixed parameters, are those quantities which define the system and which are specified as point values. In an actual case these parameters would be fixed by the geometry of the site and the properties of the fluid and waste which are relatively well known. These include the distances along the legs shown in Figure 2, the cross-sectional area of the legs, fluid properties such as density and viscosity, and waste properties such as initial inventory and half-lives. The second group, to be called variables, consists of parameters whose values are subject to uncertainties which may span several orders of magnitude. These parameters are not taken as point values in the calculation, but are approximated by distributions. These variables include solubility and retardation factors for individual radionuclides, and factors affecting groundwater travel time, such as conductivity, porosity, and hydraulic gradients. In addition, this group includes parameters which describe the Engineered Barrier System performance such as containment time by the waste packages and radionuclide release rates from the underground facility, so that repository performance can be assessed as these parameters vary.

Table 2 identifies the fixed parameters used by the model and the values used in the analyses. Table 3 identifies the variables whose values are approximated by distributions in the calculations, and gives the ranges of those values used in these analyses.

#### Input Data for Routine Release Scenario

The point values for the fixed parameters shown in Table 3 reflect the media and underground facility designs and location currently being given the most emphasis by DOE. The dimensions of the underground facility which lead to the areas of leg C and D and the length of leg C are taken \_\_\_\_\_ (Ref. x-y). The areas of legs A and B are consistent with the thickness of the Frenchman Springs Member which overlies the underground facility, and the length of leg B corresponds to the ten kilometer distance to the accessible environment. The initial radionuclide inventory is taken from DOE's projections for spent fuel (Ref. 7-8).

The variables which appear in Table 3 reflect many of the uncertainties in geohydrology including predictions of conductivities, porosities, hydraulic gradients and dispersivities. These sources of uncertainty are accounted for in the model by expressing these variables as distributions of values which span the range of available data. Similarly, distributions of solubilities and distribution coefficients ( $K_d$ 's) are used in recognition of the uncertainties involved in predicting these properties. Three radionuclides,  $^{129}\text{I}$ ,  $^{14}\text{C}$ , and  $^{99}\text{Tc}$ , do not appear to be retarded chemically, and are therefore presumed to move at the same speed as the groundwater. The bases for the data ranges and distributions are discussed below.

#### Distribution Coefficients

The selection of ranges and distributions for distribution coefficients ( $K_d$ ) in the basalt host rock and aquifer followed comparison of  $K_d$  values for basalt and basalt aquifers from the following sources: (1) Sandia National Laboratories (Ref.); (2) Golder (Ref.); (3) D. Isherwood (Ref.); and (4) DOE (SCR Ref.). It is evident upon examination of Tables 4 and 5 that there is not

a complete set of most conservative values from any one source. In all cases, however, the range of values (or value) provided by DOE overlap to some extent the value ranges from the other sources.

NRC has made the decision to proceed with the DOE values for the following reasons. The DOE values are generally in good agreement with values quoted elsewhere. The DOE values were preferred because they are well documented (RHO-BWI-LD-48), they are site-specific for the Columbia River Basalts, and they provide a complete set of the required data by the originator. Additionally, the  $3\sigma$  range for the DOE values includes a lower (hence, conservative) set of values that more closely approaches the lowest values provided by the other sources (see Tables 4, 5, and 6).

Distribution coefficient value ranges and means for Am, Pu, U, Np, and Sr in basalt given by DOE in the SCR (Ref.) for oxidizing conditions are listed in Table 6. The standard deviation for the mean value is not greater than 25% (P.F. Salter, personal communication). DOE has not provided the raw data on the  $K_d$  measurements to NRC. DOE has estimated the number of analyses for each nuclide to be approximately 8 or 9, each of which included at least three replicate analyses (P.F. Salter, verbal communication). NRC has tentatively elected to use a normal distribution for the ranges of  $K_d$  values because of the aforementioned sparsity of raw data, and because the relatively small ranges of  $K_d$  values (none greater than 1 order of magnitude) would make a log distribution inappropriate. The  $1\sigma$  range of values for Am, Pu, U, Np, and Sr in basalt host rock is listed in Table 6. These ranges are in reasonable agreement with the minimum and maximum values provided by DOE (Table 4).

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<sup>1</sup>  $K_d$  values representative of oxidizing conditions have been selected for the sensitivity analysis for conservatism.

### Solubility Limits

Because available data for elemental solubility limits is extremely limited, a range of interest was calculated for each of the following isotopes: Am, Pu, U, Np, Tc, Fission Products (Sr90, Cs137, Cs135, Sn126, Ni59, ZR93). A lognormal distribution, with endpoints representing the .001 and .999 quantiles, was assigned to each range.

The ranges were calculated in an artificial, but practical manner. Attention was directed toward fulfilling the needs of the model, and representing the values realistically.

Two factors affect the amount of radionuclides entering into solution. One is the release rate -- the number of nuclides released from the waste package per unit time.

$$R_L \leq R \leq R_u$$

where R is the release rate chosen for a particular run.  $R_L$  is the designated lower limit;  $R_u$  is the designated upper limit. For this exercise,

$$3.1 \times 10^{-6}/\text{yr} \leq R \leq 3.1 \times 10^{-3}/\text{yr}$$

The second factor is the solubility limit. This limit determines the allowable concentration of a particular element in solution.

$$S_L \leq S \leq S_u$$

where S is the elemental solubility limit chosen for a particular run.  $S_L$  is the lower limit;  $S_u$  is the upper limit. As previously stated, sufficient data is not available to provide these limits. Because of this, a range of interest was calculated for each elemental solubility.

Solubility Limits (Calculation of Su)

Su was determined to be the concentration of radionuclides in solution that is equal to the concentration that would result from the highest release rate (Ru). The equation is as follows:

$$\frac{Su \times Q}{\text{Inventory}} = Ru$$

where Q is the volumetric flow rate.

This is a valid determination of Su because the amount of nuclides entering into solution is controlled by the release rate, unless the solubility limit is exceeded. The model performs this prioritization in the following way:

if  $S \leq Su$ , then R is controlling;

for a given R, if  $S > Su$ , then Su is controlling.

Thus, Ru is the absolute upper limit for nuclides entering into solution, and the maximum solubility can be determined by

$$Ru = \frac{Su \times Q}{\text{Inventory}}$$

This calculation was performed for all of the above mentioned elements. A sample calculation, for U234, follows.

$$\begin{aligned} Ru &= 3.1 \times 10^{-3}/\text{yr} \\ Q &= K \times \text{gradient} \times \text{area} \\ &= 3.16 \times 10^{-4} \text{ ft/day} \times 1.0 \times 10^{-2} \times 8.0 \times 10^6 \text{ ft}^2 \\ &= 2.53 \times 10^1 \text{ ft}^3/\text{day} \\ \text{Inventory (at year 1000)} &= 1.46 \times 10^{32} \text{ atoms} \end{aligned}$$

$$3.1 \times 10^{-3}/\text{yr} = (\text{Su} \times 2.53 \times 10^1 \text{ ft}^3/\text{day} \times 28.32 \text{ f}/\text{ft}^3 \times 6.023 \times 10^{23} \text{ atoms/mole} \\ 1 \text{ mole}/234 \text{ g} \times 1000 \text{ g}/\text{l} \times 365 \text{ day}/\text{yr})/1.46 \times 10^{32} \text{ atom}$$

$$\text{Su} = 6.8 \times 10^{-1} \text{ g/g}$$

Values for conductivity and gradient in the flow calculation are the mean values of the ranges used in this analysis. The inventory at year 1000 is taken from ORIGEN, and represents 100,000 MTHM.

#### Solubility Limits (Calculation of $S_L$ )

The determination of  $S_L$  was based on the draft EPA limit for cumulative releases of each nuclide over 10,000 years. The equation used is as follows.

$$\text{Allowable Release} = Q \times S_L$$

The following sample calculation is for U234.

$$\begin{aligned} \text{Allowable Release} &= 10 \text{ curies}/1000 \text{ MTHM} \times 100,000 \text{ MTHM} \\ &= 1,000 \text{ curies} \end{aligned}$$

$$Q = 2.53 \times 10^1 \text{ ft}^3/\text{day} \text{ (as calculated above)}$$

$$1,000 \text{ curies} = S_L \times 2.53 \times 10^1 \text{ ft}^3/\text{day} \times 28.32 \text{ l}/\text{ft}^3 \times 1000 \text{ g}/\text{l} \\ \times 10,000 \text{ years} \times 365 \text{ day}/\text{year} \times 2.14 \times 10^{-6} \text{ curies}/\text{g}$$

$$S_L = 1.8 \times 10^{-4} \text{ g/g}$$

This value was then reduced by a factor of  $10^{-2}$ , producing a lower limit for U234 of  $1.8 \times 10^{-6}$  g/g. Because the purpose of this analysis is to provide and examine a range of interest, it was determined that a lower solubility limit that results in a release of 1% of the draft EPA standard sufficiently bounds the range of interest.

These calculations were performed on all of the above mentioned nuclides. For fission products, calculations were performed on each, and  $S_u$  for the group was determined by the highest upper limit calculated for an individual nuclide (Zr93) in the group. The value of  $S_L$  for Cs135 was chosen to represent the group of fission products because it provided the most conservative (highest) lower limit.

### Dispersivity

At the Hanford BWIP site there is only one measurement of longitudinal dispersivity, 0.8 m (2.6 ft), based on tracer tests in DC-7/8 (Leonhart and others, 1982; SCR, p. 5.1-56). While values of dispersivity measured under laboratory conditions are typically less than  $10^{-2}$  m limited data from field studies and numerical modeling of contaminant plumes indicate a range from  $10^{-2}$  to greater than  $10^{+2}$  m ( $10^{-1}$  -  $5 \times 10^{+2}$  ft) (Freeze and Cherry, 1979; S. Neaman, personal communication, 1982). Staff considers a reasonable range of dispersivity at Hanford site to be from  $10^{-1}$  to  $1.6 \times 10^{+2}$  m ( $5 \times 10^{-1}$  -  $5 \times 10^{+2}$  ft), with a lognormal distribution.

### Hydraulic Conductivity - Horizontal Leg

Measured horizontal conductivity values in the Frenchman Springs flow tops range from about  $10^{-7}$  ms ( $10^{-1}$  ft/d) to  $10^{-3}$  ms ( $10^3$  ft/d) (SCR, p. 5.1-27 - 5.1-41; Golder, 1982 a,b). To account for uncertainty in identifying the actual aquifer of interest and to account for measured horizontal conductivities which are lower than  $10^{-7}$  ms, staff recommends using a range of  $10^{-10}$  -  $10^{-3}$  ms ( $10^{-4}$  -  $10^{+3}$  ft/d). This range is generally consistent with values cited in hydrogeologic literature for basalt (Brace, 1980; Freeze and Cherry, 1979). The distribution is assumed to be lognormal.

### Porosity - Horizontal Leg

At the Hanford BWIP site there is only one measurement of effective porosity, approximately  $10^{-4}$ , based on tracer tests in DC 7/8 (Leonhart and others, 1982). When total porosity is multiplied by a factor of 0.25 to convert to

effective porosity, based on the data of NUREG/CR-2352, there is an estimated range of  $10^{-3}$  to  $10^{-1}$ . Fracture porosity/permeability relationships, such as those developed by Snow (1969), indicate a range of approximately  $10^{-4}$  to  $10^{-1}$ . Based on petrographic examination, DOE estimates the volume of unfilled fractures to be in the range of 0.025 - 0.059 volume percent ( $2.5-6 \times 10^{-4}$ ) (SCR, p. 3.5-53). Given the large uncertainty inherent in estimating a range based on only one field measurement and assuming that the range must include known measurements, staff considers a reasonable range of effective porosity to be from  $10^{-5}$  to  $10^{-1}$ . The distribution is assumed to be lognormal.

#### Hydraulic Conductivity - Vertical Leg

Vertical hydraulic conductivity values have not been measured for the Hanford BWIP site. DOE assumes a value near  $10^{-10}$  m/s ( $10^{-4}$  ft/d) based on values in the range  $10^{-12}$  to  $10^{-8}$  m/s ( $10^{-6}$  -  $10^{-2}$  ft/d) derived from regional-scale numerical modeling (MacNish and Barker, 1976; Tanaka and others, 1974). Spot measurements of horizontal conductivity from single-hole tests of dense basalts and interflows range from  $10^{-14}$  to  $10^{-8}$  m/s ( $10^{-8}$  -  $10^{-2}$  ft/d). Based on a best estimate for vertical hydraulic conductivity (Golder, 1982a) of  $10^{-9}$  m/s ( $10^{-3}$  ft/d) in dense basalts and  $10^{-8}$  m/s ( $10^{-2}$  ft/d) in interflows, staff recommends using a range of  $10^{-10}$  -  $10^{-6}$  m/s ( $10^{-4}$  -  $10^0$  ft/d) to account for uncertainty in using measured horizontal values to estimate vertical conductivity and to provide for a conservative analysis. The distribution is assumed to be lognormal.

#### Porosity - Vertical Leg

There are no measurements of effective porosity in dense basalts at the Hanford BWIP site. The range in effective porosity for the vertical leg is assumed to overlap the lower range of the horizontal leg,  $10^{-5}$  to  $10^{-3}$ , based on hydraulic conductivities and fracture porosity/permeability relationships of the dense basalts, including the DOE data cited in the SCR (p. 5.3-53). The distribution is assumed to be lognormal.

### Hydraulic Gradient - Vertical Leg

Pre-emplacment vertical hydraulic gradients based on measured heads from packed-off intervals and on measurements using the nested piezometers of DC-1 average about  $10^{-3}$ . The staff considers a reasonable range of vertical gradient to be from  $10^{-5}$  to  $10^{-2}$ , with a lognormal distribution. The vertical gradient over the dense basalts should be much higher than that over interflows (Golder, 1982a).

### Hydraulic Gradient - Horizontal Leg

Horizontal hydraulic gradients in the Frenchman Springs flow tops calculated from existing head measurements range from  $10^{-5}$  to  $10^{-3}$ . The range reflects current uncertainty in measured head values determined from packed-off test intervals (Golder, 1982a,c). The distribution is assumed to be lognormal.

### Radionuclide Release Rate

The staff selected a lognormal distribution of radionuclide release rates whose median is 1 part in 10,000 per year and whose  $3\sigma$  lower and upper bounds are 1 part in 320,000 per year and 1 part in 320 per year, respectively. This range and distribution is consistent with the performance which the staff presently estimates that DOE could provide for the engineered barrier system in the absence of a regulatory requirement on the radionuclide release time. This release rate is not expected by the staff nor forced by the model to apply to all radionuclides. Radionuclides whose solubility is sufficiently low that their release rates will be lower than the release rates selected from this distribution are modeled at whatever lower release rates are consistent with those radionuclide solubilities.

### Canister Life

The staff selected a lognormal distribution for canister life which varies from 100 to 10,000 years and whose median is 1,000 years. This distribution is selected to show the effects on repository performance of canister lives varying from the approximately 100 year lifetime associated with emplacement and retrieval through the 1,000 year lifetime which is a performance objective

in proposed 10 CFR 60 up to the 10,000 years which is the limit of the interval considered by Draft 19 of the EPA standard.

#### IV RESULTS

The effects on repository performance of the variables whose ranges appear in Table 3 were investigated by repeatedly running NWFT/DVM using a standard statistical sampling technique (Ref. 7-9, 7-10). In this statistical technique, a "case" composed of 25 values, one for each of the variables in Table 3, was selected from within the ranges shown in the table. By selecting the values at random and by running enough cases to investigate the entire data range, the effects of each of the variables on repository performance can be determined. It is important to be aware that the effects of the variables are only valid for the ranges given in Table 3. Should a variable take on a value outside the range given in Table 3, the effects of many of the variables on repository performance, as well as the overall performance of the repository might be very different.

The results described below should be interpreted with great care. This is a simple analysis which is intended to help identify potentially important parameters affecting the behavior of the Hanford site, and to demonstrate how the current uncertainties in those parameters might affect repository performance.

#### Engineered Barrier System

##### Radionuclide Release Rates

Figure 3 displays the effect of the rate of radionuclide release from the underground facility on the probability that the EPA standard for routine releases will be exceeded. It is seen that for a radionuclide release rate of about  $5 \times 10^{-6}$  per year and lower, the probability of exceeding the EPA standard is negligible. As the release rate increases, however, the likelihood of exceeding the EPA standard increases to over 70 %. This result suggests that the engineered barrier system can have a substantial impact on the likelihood

that the EPA Standard will be exceeded, and that a goal for the release rate from the engineered barrier system of about  $10^{-5}$  to  $10^{-6}$  may be appropriate to compensate for uncertainties in the geologic setting.

Figures 4 and 5 display the contributions of specific categories of radionuclides and of specific radionuclides, respectively, to the probabilities of exceeding the EPA standard shown in Figure 3. In Figure 4 it is seen that neither retarded fission products or actinides alone result in any violations of the EPA standard. This result should not be interpreted to mean that retarded fission product and actinide releases are negligible, rather that their contributions to exceeding the EPA standard are not by themselves sufficient to exceed it. The significant result of Figure 4 is that the behavior of the unretarded fission products appears to deserve the greatest scrutiny. In Figure 5 the contributions of the three unretarded fission products of greatest interest,  $^{14}\text{C}$ ,  $^{99}\text{Tc}$ , and  $^{129}\text{I}$ , to exceeding the EPA standard are displayed. It is seen that  $^{129}\text{I}$  alone does not result in any violations of the EPA standard, suggesting that the radionuclides of greatest interest at this time are  $^{14}\text{C}$  and  $^{99}\text{Tc}$ .

#### Canister Lifetime

Figure 6 displays the impact of canister life on the probability of exceeding the EPA Standard. It is seen that a canister lifetime of about 4,000 years is needed to begin to have a significant effect on repository performance. This result illustrates one of the limitations of this type of analysis. The NRC staff considers that a long lived waste package can provide significant benefits for intervals of substantially less than 4,000 years, but this viewpoint takes into consideration such effects as the thermal behavior of the engineered barrier system which is not modeled in this particular analysis.

#### Geologic Setting

##### Groundwater Travel Time

Groundwater travel time is controlled by six parameters; conductivity, porosity, and gradient in the host rock (vertical leg), and conductivity, porosity, and

gradient in the aquifer (horizontal leg). The relationship between these parameters and the groundwater travel time is straightforward:

	Host Rock	Aquifer
Groundwater Travel Time	$\frac{\text{Porosity} \times \text{Length}}{\text{Conductivity} \times \text{Gradient}}$	$\frac{\text{Porosity} \times \text{Length}}{\text{Conductivity} \times \text{Gradient}}$

From this equation and the contents of Table 3 it may readily be calculated that the median groundwater travel times in the host rock and the aquifer are about 130 years and 2,830 years, respectively, and sum to a total median travel time of about 2,950 years. Figure 7 displays the calculated distribution of groundwater travel times based on the ranges and distributions appearing in Table 3. It shows travel times on the abscissa and the probability of exceeding those travel times on the ordinate. The figure shows that there is about a 50 % probability of groundwater travel times exceeding about 4,000 years, and about a 70 % probability of groundwater travel times exceeding 1,000 years. This result could be interpreted to mean that while it is reasonably likely that the NRC groundwater travel time criterion of 1,000 years will be met, it will be necessary to make substantial reductions in the uncertainties in the above-mentioned parameters to be able to provide reasonable assurance of compliance.

The impact of the above parameters on the probability that the EPA standard will be exceeded is shown in Figures 8 through 13, respectively. The results are consistent with intuitive predictions; parameters which may vary over larger ranges of uncertainty generally appear to affect the probability of exceeding the standard more than parameters which vary over relatively smaller ranges of uncertainty. Further, there is generally more scatter at the end points of each curve than in the middle, due to the use of a lognormal distribution, which will select parameter values most frequently about the median of the distribution. Finally, the probability that the EPA standard will be exceeded appears to vary more with changes in aquifer parameters than host rock parameters because groundwater travel times in the aquifer are generally significantly greater than groundwater travel times in the host rock. The last

inference should be made with considerable caution, since contributions to exceeding the EPA standard will also depend on geochemical properties in each leg. That is, a leg with a relatively short groundwater travel time might have very good geochemical properties and thus be more important to meeting the EPA standard than a leg with relatively long groundwater travel times and poor geochemical properties.

At this time it appears to be premature even to draw conclusions about which properties of which leg deserve the most scrutiny. The uncertainties in each of the parameters are too great to confidently identify a smaller set as being particularly important.

#### Geochemistry - Solubility

Based on the radionuclides identified as most important in the Engineered Barriers discussion above, this analysis addressed technetium since carbon is presumed to be infinitely soluble. The impact of solubility on the probability that the EPA standard will be exceeded is shown in Figure 14 for technetium and in Figure 15 for the other fission products. Figure 14 might be interpreted to show that as technetium solubility approaches a maximum the probability of exceeding the EPA standard increases from about 40% to about 70%, but an examination of Figure 15 shows scatter in the results of about 20% with increase scatter around the endpoints due to the lognormal distributions. While solubility is intuitively important, in this analysis its effects appear to be obscured by other variables. This situation suggests a possible real analog; since the effects of solubility on radionuclide release rates will be coupled to groundwater flow in or near the repository, if the uncertainties in the hydrologic flow parameters needed to predict such groundwater flow are great, it may be difficult to demonstrate with reasonable assurance that radionuclide solubilities can have a significant beneficial effect on radionuclide release rates, regardless of how well solubilities are known.

#### Geochemistry - Distribution Coefficients

Figures 16 through 20 show the impacts on the probability of exceeding the EPA standard of changes in the distribution coefficients in the host rock and in the aquifer for americium, plutonium, uranium, neptunium, and the retarded fission products, respectively. Although none of these retarded radionuclides alone result in exceeding the EPA standard, it is theoretically possible that they may make partial contributions to exceeding it. In fact it is seen that for americium and uranium distribution coefficients in the aquifer (Figures 16b and 18b), and for the neptunium distribution coefficient in the host rock (Figure 19a), there are no cases which exceed the EPA standard for the upper portions of these ranges. This result may suggest that these parameters be emphasized in future geochemical investigations. On the other hand, the single value in the plutonium distribution coefficient in the aquifer (Figure 17b) may be an artifact of the sampling technique which, as mentioned earlier, generally causes more scatter at the end points of each curve than in the middle, due to the use of, in this case, a normal distribution.

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NOTE ON DRAFT 1. ANALYSES OF GEOCHEMICAL PARAMETERS WHICH INCLUDE TABULATED NUMERICAL RESULTS WILL BE ATTEMPTED FOR INCLUSION IN DRAFT 2.

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## V ANALYSIS OF THE IMPACT OF FAILED SHAFT AND BOREHOLE SEALS

### Introduction

This performance assessment analysis was undertaken to evaluate the importance of failed borehole plugs and shaft seals in the effective containment of radionuclides by a High-Level Nuclear Waste Repository. The principal objective of long term repository performance assessment is to quantify the releases of potentially hazardous radionuclides to the accessible environment. The performance assessment detailed herein evaluates groundwater flow paths and travel times and the effects of various input parameters on these dependent characteristics of the physical system. An updated version of the one-dimensional, network, radionuclide transport code, NWFT/DVM (ENGDVM) is

used to evaluate the sensitivity of repository models in basalt to the hydraulic characteristics of shafts with failed seals. Specific parameters investigated include hydraulic conductivities, porosities, hydraulic gradients, and path lengths of groundwater flow to the accessible environment. The input parameters that characterize the host rock and aquifers in the basalt system are also analyzed to vary the importance of the shafts with failed seals throughout the analysis.

In the basalt system of the Pasco Basin, Washington, groundwater will eventually transport harmful radionuclides to discharge points within the biosphere. Prior to licensing a High-Level Waste Repository at Hanford, Washington, the NRC must convince itself and the public that these releases will not have significant impacts on the neighboring ecological systems. By prolonging the release of the pernicious radionuclides to the accessible environment, the impact of the releases will be reduced since the radionuclides continue to decay to lower activity levels through time. Investigators for the Department of Energy (DOE) are attempting to prove that sufficient time will pass prior to the initial release of radionuclides to the environment so that these releases will be inconsequential. DOE proposes sites to be High-Level Waste (HLW) repositories because they believe that the natural barriers (e.g. long groundwater travel times, highly sorptive host rocks, low hydraulic gradients, long term geologic stability, etc.) and engineered barriers (e.g. waste packages, mined repository, waste form, etc.) will sufficiently prevent early releases of the radionuclides to the accessible environment.

The rationale for the multiple barrier approach and the scientific basis for HLW geologic repositories is discussed in Chapter 12 of the Site Characterization Report (SCR) for DOE's proposed repository at Hanford, Washington. To avoid redundancy, this discussion excludes the rationale. Chapter 12 also discusses the technical criteria that must be satisfied by a proposed repository system prior to licensing of the facility by the U.S. Nuclear Regulatory Commission (NRC). The principal technical criterion, proposed by the NRC, is that the minimum groundwater travel time from the repository to the accessible environment 10 kilometers distant be in excess of 1000 years. The U.S. Environmental Protection Agency (EPA) has also proposed

limitations on the releases of radionuclides at a similar border zone in several drafts of a proposed standard. In the belief that these standards will eventually become law through actions of the EPA, the NRC also evaluates the performance of proposed repositories by their ability to comply with these standards. The following sensitivity analysis evaluates the compliance of a model repository in the Pasco Basin Basalt System to these draft standards and stresses the dependence of groundwater travel times and discharges of radionuclides on the hydraulic conductivities, porosities, and hydraulic gradients along the flow path between the repository and the accessible environment. The importance of failed shafts in potential release scenarios will also be analyzed.

### Sensitivity Analysis

This paper documents the current status of the modeling of the borehole/shaft seal failure scenarios performed by NRC staff in the Performance Assessment Section of High-Level Waste Management Licensing Branch of the Office of Nuclear Materials Safety and Safeguards. Since many of the parameters used in the sensitivity analysis are representative of the basalt system of BWIP at Hanford, Washington, these analyses illustrate the importance of groundwater flow system variables at Hanford in determining groundwater travel times, flow paths, and discharges of radionuclides to the accessible environment.

Before commencing the computer modeling program of this sensitivity analysis, the flow system can be evaluated qualitatively to determine the relative importance of flow variables. Darcy flow is assumed throughout the system, and so the dependence of the darcy velocity on the hydraulic gradient and conductivities is obvious from the inspection of the algebraic expression of Darcy's Law,

$$Q = KIA, \text{ or}$$

$$Q/A = u = KI, \text{ where}$$

Q is the volumetric flow rate; A is the cross-sectional area of the flow path; K is the hydraulic conductivity; I is the hydraulic gradient; and u is the darcy velocity. Naturally these variables must have consistent units, or else conversion factors are required to satisfy the equation. Since the darcy velocity describes flow through an equivalent porous medium, this velocity does not accurately describe the median velocity of groundwater. To account for tortuosity of the flow path as water migrates through individual pores, the darcy velocity must be divided by the effective porosity. Effective porosity ignores pores that are not interconnected as water cannot appreciably flow through the solid framework of the porous medium. Thus an average linear velocity of groundwater flow may be calculated as

$$v = u/en, \text{ where}$$

n is the effective porosity, v is the average velocity of groundwater flow, and e is an empirical constant dependent on the characteristics of the porous medium. To calculate groundwater travel times along any specified flow path, one merely needs to divide the distance along the flow path by the average velocity, once again assuming the units are consistent. If the average velocity varies systematically along the flow path, then a simple flow path must be divided into segments along which the average velocity is constant. In this situation, the travel time will be the sum of the individual travel times along the segments of the flow path. Should the average velocity inconsistently vary along the flow path, or the flow path cannot be discretized into segments along which the velocity is nearly constant, then the travel time must be integrated along the flow path. By using a simple network flow system in the sensitivity analysis, integration of the velocities is not necessary as they are constant for any given leg of the system.

Since this sensitivity analysis is one-dimensional, hydraulic parameters like conductivity and porosity can only vary along the flow path. This assumes that a one-dimensional model of the flow system is valid and that the rocks along the flow path may be characterized as homogeneously conductive and porous materials. These assumptions are also implicit in the application of the

NWFT/DVM model used in the analysis. The flow system can be discretized into representative flow lengths or legs along the path length that can be characterized by a corresponding hydraulic conductivity and porosity.

Inspection of the equation used to calculate groundwater travel times illustrates the proportionality of travel time to effective porosity and path length and its inverse proportionality to hydraulic gradient and conductivity, or

$$t_i = (L_i n_e) / (K_i I_i), \text{ where}$$

$t_i$  is the mean groundwater travel time along leg  $i$ , and  $L_i$  is the path length of leg  $i$ . Based on this relationship, increasing the porosity or path length for a particular leg or decreasing the hydraulic conductivity or gradient would increase the groundwater travel time for that leg. Although the value of  $e$  is approximately 1 for uniformly packed sands, its value in fractured media, including basalt, is unknown. The total travel time along the flow path may be calculated by summing the travel times of all the flow legs, or

$$T_t = \sum t_i, \text{ where}$$

$T_t$  is the total mean travel time along a given flow path composed of  $n$  legs. This approach permits the calculation of different groundwater travel times for alternate flow paths in more complex models if the average velocities of groundwater flow are known for these flow legs.

To summarize this qualitative analytical approach to the sensitivity analysis of the failed borehole/shaft seal scenario, the following predictions about the sensitivity of the system to various input parameters can be made:

(1) travel times increase if any of the porosities of the rock units along the flow path from the repository to the accessible environment increase,

(2) travel times increase if the path length from the repository to the discharge point increases,

(3) travel times decrease if any of the hydraulic conductivities of the rock units along the flow path from the repository to the discharge point increase, and

(4) travel times decrease if the hydraulic gradients along the flow path from the repository to the discharge point increase.

These predictions are simple interpretations of Darcy's Law and the equation for groundwater travel time. The relative importance of the empirical constant,  $e$ , in calculating the average groundwater velocity is presently unknown (Freeze and Cherry, 1979). In fractured media like the basaltic host rocks at Hanford, groundwater flow predominantly occurs along fractures that serve as conduits for transport. As these fractures provide a more direct route for groundwater migration, the tortuosity along the flow path is considerably less than that of water flowing through a uniformly porous medium. The roughness of the fracture may contribute some tortuosity to the flow, but this would be relatively insignificant compared to the deviations of flow that occur between individual pores. More uncertainty is included in this term since flow through fractures may be turbulent rather than laminar. These uncertainties in the value of  $e$  for fractured media force the assumption that the basalt system behaves as an equivalent porous medium; the constant  $e$  equals 1. The validity of this assumption is questionable.

The validity of all the assumptions made in this sensitivity analysis and the accuracy of these predictions will be evaluated by comparison with the results of the NWFT/DVM modeling program detailed below. Prior to a complete description of this program, however, several comments should be made concerning the use of the updated version of NWFT/DVM (ENGDVM). NWFT/DVM was selected to model these one-dimensional failure scenarios as it is the only radionuclide transport code currently being used by the Performance Assessment Section of WMHL. The current version of NWFT/DVM is limited in its application to sensitivity analyses of the borehole/shaft seal failure scenarios. This limitation, caused by the required specification of groundwater flow path through the network prior to execution, may cause the program to ignore a altered input parameter if this variable is changed in a leg that is not

included in the specified flow path. Removal of this requirement would greatly expedite the sensitivity analysis of the scenarios, but it would also decrease the computational efficiency of the program, thus increasing execution costs.

In the present sensitivity analysis of borehole/shaft seal failure scenarios, input parameters are independently substituted into the basecase scenario that has a specified flow path along legs 13,12,7,14 and 4. All the legs of the NWFT/DVM network model are shown in Figure 21. Parameters that controlled the importance of the failed shaft (leg 10) in the model were then substituted into a similar basecase scenario where the flow path was specified as 13,10,3, and 4. Since the model is sensitive to the hydraulic conductivities and gradients of the flow legs and the changing of these parameters causes a variation in the dominant flow path, many of the input parameter sets were repeated using both specified networks to thoroughly evaluate their effect on the system.

#### Description of the Flow System

The standard NWFT/DVM network consists of 15 legs that simulate flow through an underlying aquifer, faults, repository tunnels, host rocks, shafts, and/or an overlying aquifer that conduct repository effluents to a discharge point at the end of leg 4. The basic network including the legs and leg junctions is shown in Figure 21. The basecase scenario is pictured in Figure 23 and can be seen to be a variation of the basic network. The legs of the basecase scenario and their physical analogs are listed below:

<u>Leg Number</u>	<u>Model Counterpart</u>
1	Pipe
2	Upper Aquifer
3	Pipe
4	Upper Aquifer
5	Pipe
6	Lower Aquifer/Aquitard

7	Pipe
8	Lower Aquifer/Aquitard
<u>Leg Number(continued)</u>	<u>Model Counterpart</u>
9	Failed Shaft
10	Failed Shaft
11	Host Rock below Repository
12	Host Rock above Repository
13	Repository
14	Pipe
15	Aquitard/Pipe

The pipes in the model merely serve to conduct groundwater into the model and to simulate vertical migration up through leg 12, the host basalt above the repository. They are generally highly conductive, short, narrow, and have a low porosity. Water that migrates up leg 10 must travel through leg 3, which is 100 feet long to reach the discharge portion of the network, leg 4. Correspondingly, groundwater that flows down leg 12 must travel through pipes 7 and 14, which sum to 200 feet long, to reach the discharge portion of the model. Since junctions 9 and 11 have been given the same elevations as the junctions in the upper aquifer, the basecase scenario models both flow up the failed shaft and through the basalt overlying the repository. It should be noted, however, that the path length through the host basalt is 100 feet longer than the flow path through the failed shaft. This disparity in flow path lengths will naturally increase the groundwater travel time through the host basalt compared to the failed shaft.

To evaluate the validity of the parameters which were input into the basecase model, the characteristics of legs 10 and 12 are listed below. A complete listing of the input parameters for all legs in the network may be found in Figure 23. The physical characteristics of leg 10, the failed shaft, are as follows:

Length = 1500 feet,

Cross-sectional Area = 300 sq. feet,  
Hydraulic Conductivity =  $7.3E2$  feet/year or 2 feet/day ( $7E-6$  m/s),  
Porosity = 0.25 (fraction).

In comparison the physical characteristics of leg 12, the overlying basalt, are as follows:

Length = 1500 feet,  
Cross-sectional Area = 8,000,000 sq. feet,  
Hydraulic Conductivity =  $1E-6$  feet/year ( $3.5E-11$  m/s), and  
Porosity =  $3.2E-4$  (fraction).

All of the input parameters may be compared for validity with similar characteristics provided by DOE, EPA, Golder Associates, and the parameter ranges found in the Rationale for the Performance Objectives found in 10 CFR 60 by the NRC. Many of the original input parameters were decided upon by NRC Performance Assessment Staff and contractors. Hydrochemical Parameters

Since the release scenarios of radionuclides are extremely sensitive to solubility limits, the limits are usually not enforced to make the model more sensitive to changes in the independent parameters. Distribution coefficients and the dispersivity remain constant throughout this analysis so that the only geochemical parameter varied in the computer models is the enforcement of solubility limitations. The solubility limits used in this analysis are listed in Table 9. NRC staff believe these values to be current estimates of the solubilities of the dominant radionuclides in the representative repository. The accuracy of these values is being examined in a sensitivity analysis that is being conducted independently of this study.

The validity of the assumption that these values do represent the actual solubilities of several radionuclides cannot be defended within the scope of this analysis. Since many of the laboratory experiments and theoretical analyses that determined these parameters were conducted under the assumption of chemical environments within bedded salt deposits, their application in the hydrochemical environments within the basalts in the Pasco Basin is

questionable. Nevertheless, they do effectively limit the release and transport of radionuclides away from the repository; a solubility-limited release scenario is certainly more plausible than the ultraconservative leach-limited approach. Previous analyses of release scenarios through failed shaft seals have indicated that solubility limits are important in controlling the accumulative discharge to the accessible environment (Lester, Thomas, and Faust, 1982).

Leach time in all models begins 50 years after the completion of the repository and continues for 100,000 years. The radionuclide inventory at 50 years is included in the listing below:

<u>Radionuclide</u>	<u>Amount at 50 years</u>
C14	6.39E4 ci,
Ni59	2.28E5 ci,
Sr90	1.09E9 ci,
Zr93	1.91E5 ci,
Tc99	9.41E5 ci,
Sn126	3.49E4 ci,
U234	7.22E4 ci,
Pu239	2.28E7 ci, and
Pu240	3.33E7 ci.

The dispersivity (lateral), which remains constant in all scenarios, is 50 feet. To avoid numerical oscillation and overshoot/undershoot errors in the execution of the models, the minimum length of any leg in the network was assigned the value of 100 feet. The pipes that connect the upper and lower aquifers with the repository, shafts, and host basalt are characterized by this path length.

The distribution coefficients of the radionuclides within the various porous media of the model also remain constant in every scenario. If the flow path is altered from that of 13-12-7-14-4 to 13-10-3-4, the groundwater effluent from the repository encounters different units along the flow path.

Discharges to the accessible environment will vary for the different pathways due to disparities in travel times and sorption characteristics of the conducting rocks. Distribution coefficients are required by NWFT/DVM for each of the legs within the specified flow path. By changing the flow path, one must also change the distribution coefficients. While many of the sorptive characteristics are the same for a given radionuclide in different materials, the distribution coefficients may change dramatically depending upon the host material.

An example of this phenomenon may be seen in the difference of sorptive characteristics of C14 in cement as compared to basalt. In this sensitivity analysis, transport of C14 is not retarded in basalt. In contrast, transport of C14 is significantly retarded in flow through cement. These findings are included in several draft documents prepared for the NRC by its contractors, so they cannot be referenced in this document. The validity of this behavior cannot be defended within the scope of this analysis. Based on this behavior of C14, a qualitative prediction would expect that C14 will escape much more easily to the accessible environment when the groundwater flows through basalt rather than the cement-filled, failed shaft. A complete listing of the retardation factors and distribution coefficients for each leg along the pathway is included as Table 10.

The source of all the radionuclides is a 50 year old repository that is 620 feet long. The tunnels in this repository have a total cross-sectional area of 104 square feet. Other flow characteristics for the repository tunnels are detailed in Figure 22. The computer code ORIGEN supplies the initial radionuclide inventory for a 100,000 MTHM repository. This inventory naturally changes during the fifty years prior to initial leaching of the waste because of radioactive decay. The inventory of radionuclides at the time of initial leaching has been previously listed. Description of the Basecase Scenario

In the basecase scenario, a geologic repository for HLW is located 1500 feet below an overlying aquifer. Groundwater flowing through this aquifer discharges ten kilometers distant from the surface projection of the repository so that any radionuclides released from the repository will be released to the

accessible environment where this aquifer discharges into a river. In the case of the proposed repository at Hanford, this aquifer represents the more transmissive zones of the Frenchman Springs Member of the Wanapum Basalt in the Pasco Basin. The repository horizon is modeled within the dense flow interior zone of the Umtanum Basalt Flows below the Frenchman Springs Member. An underlying aquifer supplies groundwater to the repository through the host basalt in which the repository has been constructed. This groundwater flow represents the regional flow that may exist beneath the proposed facility that occurs within the more conductive zones of the Pre-Columbia River Basalt Group.

Groundwater flowing through this lower aquifer-system flows into the repository through the basalt from below. Although the system may be connected along lineaments, fractures, and faults, the occurrence of this upward migration is not predicated upon their existence. The physical characteristics of this leg, leg 11, are similar to those of leg 12, the overlying basalt. The repository also receives groundwater from the aquifer system above. This connection is along the access shafts constructed along with the mined repository and sealed after completion. Subsequent to their effective sealing, the shafts begin to conduct appreciable volumes of water so that the hydraulic conductivities of the shafts increases to 2.0 feet/day as the seals degrade. Since groundwater essentially flushes into the repository from above and below and then discharges back into the upper aquifer, the entire flow system may be conceptualized as a modified U-tube scenario. These scenarios were popularized during the preliminary performance assessment of HLW repository strategies in bedded salt deposits.

The groundwater in this U-tube scenario is entirely driven by hydraulic gradients. All thermal and brine effects have been neglected. Maximum temperatures expected in the near-field surrounding a repository will cause a density difference of several percent as the water absorbs heat and expands. The effects of the increase in temperature on the water viscosity is much more significant and may decrease the viscosity by 20 to 30 times (SCR, Chapter 12, 1982). In spite of this dependence of both the viscosity and density of the groundwater on temperature in the near-field, temperature effects are ignored since they will probably be damped out in the far-field as considered in this

study. Water migration induced by density differences between freshwaters and brine have been neglected because no brines have been identified within the Pasco Basin groundwater flow system.

The hydraulic gradients chosen for the basecase simulate actual gradients measured across the repository site (see Table I). These gradients are enforced throughout the model by specifying the input and output pressures at junctions 1, 2, and 3. Early runs conducted to establish the basecase indicated that the model is quite sensitive to changes in the input pressures and consequently, hydraulic gradients. Input pressures were calculated using symbolic head values to yield the gradients of  $5E-4$  ft/ft laterally in the Frenchman Springs Member and  $1E-2$  ft/ft vertically between the Pre-Columbia River Basalts and the Frenchman Springs Formation. The output pressure at junction 3 is assigned the pressure of 0.0 psi since the aquifer discharges to the river, and atmospheric pressure equals zero.

Groundwater, driven by these gradients and pressures, flows up leg 11 (the underlying host basalt) and down leg 9 (a shaft with failed seal), through leg 13 (the repository), and into leg 10 (another shaft with a failed seal) and leg 12 (the overlying host basalt). Flow from legs 10 and 12 eventually discharges into leg 4, the overlying aquifer. This leg is 10 km long, so its discharge point represents the border zone specified in the EPA and NRC draft regulations around a HLW repository through which the total discharge of radionuclides is limited. Although a flow path of 13-12-7-14-4 is usually specified in the computer runs, groundwater in the model is not restricted to this path. Groundwater flows, therefore, through both the failed shaft and the overlying basalt. Although the shaft is generally much more conductive than the basalt, flow through the shaft is restricted by its small cross-sectional area.

#### Results of Computer Modeling Program and Conclusions

This limitation of groundwater flow from the repository into the failed shaft is only one of the many factors warranting consideration in reviewing the results of the computer analyses. When the conductivities of the failed shafts

are within plausible limits, shaft conduction is limited to a maximum rate. Effluent from the repository that cannot flow through the failed shaft is forced through the host basalt. Although the shaft generally represents the most rapid flow path to the accessible environment, the volumes of groundwater flow discharged into the overlying aquifer are limited. This limitation of volume also limits the discharge of radionuclides from the repository to the biosphere. Many of the radionuclides that will be transported in the repository effluent may be sorbed onto the host basalt, if most of the groundwater discharge is forced through the overlying rock. The failed shaft generally represents the flow path characterized by the minimum travel time for a given set of input parameters and should, therefore, be considered as an important repository breachment scenario.

The results of the 45 scenarios analyzed in this sensitivity analysis have been summarized in Table 8. This table provides the reader with an abbreviated run title, parameters altered with respect to the basecase, minimum and mean groundwater travel times, percentage of repository effluent funneled into leg 12, an indication of the radioisotopes released to the accessible environment from the repository, and remarks about the validity of the particular scenario. Many of the computer runs were executed without enforcing the solubility limits on the radionuclides. These runs produced a more detailed estimate of the sensitivity of the particular model to altered input parameters. Several of the less instructive computer models have been deleted from this listing.

Figure 24 also summarizes the minimum travel times calculated from the results of this modeling program. Eight models calculated minimum groundwater travel times less than 20,000 years, and three of these had travel times less than 10,000 years. No models were executed that calculated travel times less than 1000 years, the NRC technical criterion concerning minimum groundwater travel times. Several models exceed the proposed EPA standards for the release of radionuclides from HLW repositories. These models are indicated in Table 8. The three models with minimum groundwater travel times less than 10,000 years should be examined to determine the important parameters that effectively decreased the groundwater travel times values below the absolute minimum groundwater travel times stated in the SCR.

Run 2X yields the least minimum groundwater travel time of 1900 years from the repository to the discharge point 10+ km distant. This model incorporates relatively high hydraulic conductivity values for the host basalt along with elevated lateral and vertical hydraulic gradients. These values were selected from the 1981 draft of Population Risks from Disposal of High-Level Radioactive Wastes in Geologic Repositories by the EPA. The lateral gradient through the Frenchman Springs is assumed to be .01 ft/ft, and the vertical gradient through the repository is assigned as 0.1 ft/ft. A value of  $2.8E-2$  ft/day is assumed as the hydraulic conductivity of the host basalt. While the input conductivity for the basalt and the lateral gradient are possible, the elevated vertical gradient is highly improbable (NRC, 1981). Even though solubility limits are enforced in this model, the discharge of radionuclides exceeds the EPA draft standard.

Another EPA scenario, Run 3F maintains the same vertical and lateral hydraulic gradients and the same hydraulic conductivity of the basalt, while increasing the porosities of the basalt and the overlying aquifer. These changes decrease the travel time from the minimum travel time calculated in the basecase scenario as 10,268 years to 7585 years. Since the same hydraulic gradients are used in both models 2X and 3F, the results of model 3F are of questionable validity since the vertical gradient specified exceeds the maximum probable vertical hydraulic gradient by an order of magnitude. It is also important to note that in these two models, flow occurs down leg 10, the failed shaft. The upper aquifer drains into the repository through legs 9 and 10. The groundwater flowing in leg 10 funnels into leg 12 so that leg 12 conducts over 200% of the groundwater flow through the repository.

In model 3D, the other model with a groundwater travel time less than 10,000 years, the hydraulic conductivity is reduced to  $2.8E-6$  ft/day. In addition, the parameters that have been altered from the basecase scenario in models 2X and 3F have been similarly altered in this model as this is another EPA scenario. The validity of this model is also questionable because of the anomalously high vertical gradient that is used, which is not representative of the physical system. Although the computed travel times and discharges of radionuclides to the accessible environment may not be realistic, these models

do illustrate the dependence and sensitivity of groundwater velocities on hydraulic gradients. This result supports the earlier prediction that groundwater travel times decrease as the hydraulic gradients along the flow path increase.

Similar conclusions may be drawn from the review of the other computer models with longer minimum groundwater travel times. By comparing the effects on the minimum groundwater travel times by the varied input parameters, the sensitivity of the borehole/shaft seal failure scenario can be quantified. This comparison also illustrates the importance of the borehole/shaft seal failure as a viable release scenario that challenges the integrity of a geological repository for HLW in the basalt system at Hanford, Washington. The conclusions drawn from these comparisons include:

- o the model is sensitive to changes in the porosity of the overlying aquifer; the travel time along the flow path is linearly proportional to this porosity as predicted by Darcy's Law;

- o the model is sensitive to changes in the path length of repository effluent to the discharge point; the travel time is linearly proportional to the path length as predicted by Darcy's Law;

- o the model is sensitive to changes in the hydraulic gradients present in the pathway between the repository and the discharge point; travel time is inversely proportional to the hydraulic gradient as predicted by Darcy's Law;

- o the model is sensitive to changes in the hydraulic conductivities of the porous media between the repository and the discharge point; travel time is inversely proportional to these hydraulic conductivities as predicted by Darcy's Law;

- o the model is not sensitive to changes in input parameters that describe the flow system prior to the flow path's interception of the repository, for a given distribution of hydraulic head throughout the system; if these input

parameters are varied, and they cause another distribution of hydraulic head throughout the system, then the travel time will be sensitive to these changes;

- o the failed shaft is an effective short circuit to the flow system through the host basalt and may conduct effluent from the repository much more rapidly to the overlying aquifer than through the basalt;
- o radionuclide discharge through the failed shaft is largely controlled by the solubility of the waste species, their distribution coefficients within the fill material used in the shaft, and the conductivity contrast between the host rock and the shaft;

- o groundwater travel times through the failed shaft can be minimized by filling the shaft with a material characterized by a low hydraulic conductivity and a very high porosity; and

- o shafts with failed seals may effectively short circuit the flow path reducing groundwater travel times significantly below the 37,000 year absolute minimum proposed by DOE for the intended repositories at Hanford, Washington.

#### Limitations of this Analysis

The conclusions stated above are predicated on the following assumptions:

- o that porous media flow calculations are valid in estimating groundwater flow through the shaft seals, shaft-seal interfaces, and disturbed zones surrounding the shaft;

- o that single differential heads represent the natural distribution of heads through the entire shaft;

- o that flow can be effectively modeled for this system by a one-dimensional, isothermal, steady-state, network radionuclide transport code;

o that the hydraulic conductivities assigned to the failed shafts accurately represent the effective hydraulic conductivities of the shaft-seal-disturbed zone system;

o that the solubilities, distribution coefficients, and initial inventories are representative of the physical repository system; and

o that the empirical constant  $e$  in the average linear velocity calculation is effectively equal to 1 in the fractured basalt system.

If these assumptions are invalid for the flow system within the Pasco Basin at the Hanford Site, then the results computed here cannot be applied directly in the performance assessment of BWIP. The general results of this study can be applied, however, to virtually any groundwater flow system where groundwater migration obeys Darcy's Law.

Table 1

Limits of Cumulative Releases to the Accessible Environment for 10,000 Years After Disposal According to the Assumed Standard

<u>Radionuclide</u>	<u>Release Limit Curies Per 1000 MT</u>
Americium-241	10
Americium-243	4
Carbon-14	200
Cesium-135	2000
Cesium-137	500
Neptunium-237	20
Plutonium-238	400
Plutonium-239	100
Plutonium-240	100
Plutonium-242	100
Radium-226	3
Strontium-90	80
Technetium-99	2000
Tin-126	80
Any other alpha-emitting radionuclide	10
Any other radionuclide which does not emit alpha particles	500

NOTE: In cases where a mixture of radionuclides is projected to be released, the limiting values shall be determined as follows: For each radionuclide in the mixture, determine the ratio between the cumulative release quantity projected over 10,000 years and the limit for that radionuclide as determined from Table 2. The sum of such ratios for all the radionuclides in the mixture may not exceed one.

For example, if radionuclides A, B, and C are projected to be released in amounts  $Q_a$ ,  $Q_b$ , and  $Q_c$ , and if the applicable Release Limits are  $RL_a$ ,  $RL_b$ ,  $RL_c$ , then the cumulative releases over 10,000 years shall be limited so that the following relationship exists:

$$\frac{Q_a}{RL_a} + \frac{Q_b}{RL_b} + \frac{Q_c}{RL_c} \leq 1$$

TABLE 2. FIXED PARAMETERS FOR ROUTINE RELEASE

<u>Description</u>	<u>Value</u>	<u>Units</u>
Area of leg A	$6 \times 10^6$	ft <sup>2</sup>
" " " B	$6 \times 10^6$	"
" " " C	$8 \times 10^6$	"
" " " D	$8 \times 10^6$	"
Length of leg A	Not needed	ft —
" " " B		"
" " " C	15	"
" " " D	1500	"
Conductivity of leg C	infinite	
Porosity of leg C	Not needed	
Pressure at point 1	0	psi
Initial radionuclide inventory	*	Curies
Radionuclide half lives	*	years

\*From Ref. 7-7

Table 3

Variables and their ranges. (For normal and lognormal distributions, ranges are for .001 and .999 quantiles)

Variable	Distribution	Range	Units
Kd for Am in host rock	Normal	8.5E1 - 6.0E2 <sup>(1)</sup>	ml/g
Kd for Pu in host rock	Normal	5.0E0 - 3.9E1 <sup>(1)</sup>	ml/g
Kd for U in host rock	Normal	1.0E0 - 1.1E1 <sup>(1)</sup>	ml/g
Kd for Np in host rock	Normal	2.0E0 - 1.8E1 <sup>(1)</sup>	ml/g
Kd for fission products in host rock	Normal	4.2E1 - 3.0E2 <sup>(1)</sup>	ml/g
Kd for Am in aquifer	Normal	2.5E2 - 1.8E3 <sup>(1)</sup>	ml/g
Kd for Pu in aquifer	Normal	5.0E2 - 3.5E3 <sup>(1)</sup>	ml/g
Kd for U in aquifer	Normal	1.8E1 - 1.2E2 <sup>(1)</sup>	ml/g
Kd for Np in aquifer	Normal	1.2E1 - 8.8E1 <sup>(1)</sup>	ml/g
Kd for fission products in aquifer	Normal	5.0E1 - 3.5E2 <sup>(1)</sup>	ml/g
Solubility limit for Am	Lognormal	1.2E-12 - 8.1E-6 <sup>(2)</sup>	g/g
Solubility limit for Pu	Lognormal	1.5E-10 - 4.3E-3 <sup>(2)</sup>	g/g
Solubility limit for U	Lognormal	1.8E-6 - 6.8E-1 <sup>(2)</sup>	g/g
Solubility limit for Np	Lognormal	1.1E-8 - 1.1E-3 <sup>(2)</sup>	g/g
Solubility limit for Tc	Lognormal	4.5E-8 - 6.5E-4 <sup>(2)</sup>	g/g
Solubility limit for fission products	Lognormal	6.6E-7 - 5.6E-4 <sup>(2)</sup>	g/g
Dispersivity	Lognormal	5.0E-1 - 5.0E2 <sup>(3)</sup>	ft
Radionuclide release time	Lognormal	3.2E2 - 3.2E5 <sup>(4)</sup>	yr
Conductivity in aquifer (legs A & B)	Lognormal	1.0E-4 - 1.0E3 <sup>(3)</sup>	ft/day
Porosity in aquifer (legs A & B)	Lognormal	1.0E-5 - 1.0E-1 <sup>(3)</sup>	--
Conductivity in host rock (legs C & D)	Lognormal	1.0E-4 - 1.0E0 <sup>(3)</sup>	ft/day
Porosity in host rock (legs C & D)	Lognormal	1.0E-5 - 1.0E-3 <sup>(3)</sup>	--
Gradient in host rock	Lognormal	1.0E-5 - 1.0E-2 <sup>(3)</sup>	ft/ft
Gradient in aquifer	Lognormal	1.0E-5 - 1.0E-3 <sup>(3)</sup>	ft/ft
Canister life	Loguniform	1.0E2 - 1.0E4 <sup>(5)</sup>	yr

Table 4  
 Distribution Coefficient Values  
 for Basalt (ml/g)

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	Sandia	Golder	Isherwood	DOE
Am	25-2 x 10 <sup>6</sup>	500	70-280	340 (230-600)
Pu	45-5200	50	2 X 10 <sup>4</sup> (Fried) 60-100 (Seitz)	22 (20-25)
U	4-1300	3	-	6 (1-15)
Np	1.5-2800	5	-	10 (7-42)
Sr	-	-	-	170

Table 5  
Distribution Coefficient Values  
 for Basalt Aquifers (ml/g)

	Sandia	Golder	Isherwood	DOE*
Am	.01 - 100,000	117	8-11 (Seitz)	1000
Pu	.01 - 10,000	100	20-64 (Seitz)	2000
U	.01 - 10,000	500	-	70
Np	.01 - 50	5	-	50
Sr	-	-	-	200

\* Kd value representative of secondary minerals in basalt

Table 6  
 Distribution Coefficients (Measured Under  
 Oxidizing Conditions) for Columbia River Basalt  
 Geohydrologic System (ml/g)

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<u>Nuclide</u>	<u>DOE</u>	<u>Basalt</u>		<u>DOE</u>	<u>Secondary Minerals</u>	
		<u>1<math>\sigma</math> Range</u>	<u>3<math>\sigma</math> Range</u>		<u>1<math>\sigma</math> Range</u>	<u>3<math>\sigma</math> Range</u>
Am	340	255-425	85-595	1000	750-1250	250-1750
Pu	22	16.5-27.5	5.5-38.5	2000	1500-2500	500-3500
U	6	4.5-7.5	1.5-10.5	70	52.5-87.5	18-120
Np	10	7.5-12.5	2.5-17.5	50	37.5-62.5	12-88
Sr	170	127.5-212.5	42.5-297.5	200	150-250	50-350

TABLE 7 COMPARISON OF INPUT PARAMETERS

Source of Parameters:	<u>BC</u>	<u>Golder</u>	<u>EPA</u>	<u>DOE</u>	<u>10 CFR 60</u>
Parameter:					
Hydraulic Conductivity (ft/day)					
Host Basalt	1E-3	1.13E-2	2.8E-2 - 2.8E-6	<2.83E-6 - 2.8E-8>	<1-1E-7>
Upper Aquifer	0.19	--	0.28	<2.83E2 - 2.8E-3>	<1E4-1>
Repository	0.1	2.83E2	0.1	--	--
Shaft	2.0	<2.8E1 - 2.83E-3>	2.0	<2.83 - 2.83E-8>	--
Porosity (fraction)					
Host Basalt	3.2E-4	1E-2	1E-2	--	<1.1E-1 - 1.1E-3>
Upper Aquifer	1E-2	--	0.15	<1E-1 - 1E-2>	<3E-1 - 1E-1>
Repository	0.5	3E-1	0.50	0.25	--
Shaft	0.25	5E-2	0.25	0.25	--
Hydraulic Gradients					
Lateral	5E-4	7.3E-3*	0.01	8E-4	<1E-2 - 1E-4>
Vertical	1E-2	7.2E-3*	0.01	7.3E-2	<3E-2 - 5E-3>

\*Calculated using path lengths of basecase.

BC = Base case scenario

Golder = Draft tunnel seal failure analysis

EPA = Draft rationale document for proposed standard, 1981

DOE = Status reports, September, 1982, and conceptual design description (RHO-BWI-C-116)

10 CFR 60 = Rationale for performance objectives of 10 CFR 60 - 1981 - NRC

TABLE 8 | INPUT PARAMETERS AND MINIMUM GROUNDWATER TRAVEL TIMES

Run Number	Input Parameter Varied	Minimum Groundwater Travel Time (yrs)	Average Groundwater Travel Time (yrs)	Percent of Repository Flow Through Leg 12 (%)	Solubility Limits Enforced	Discharge of Radionuclides Exceeds EPA Draft Standard	Remarks
2X	$P_1 = 145.25\text{psi}$ $P_2 = 955.6\text{psi}$ $K_{11} - K_{12} = 2.8E-2$	1,390	1,905	225	yes	yes	EPA Scenario
3D	$P_1 = 145.25$ $P_2 = 955.6$ $n_2 = n_4 = .15$ $K_{11} = K_{12} = 2.8E-6$ $n_{11} = n_{12} = 1E-2$	8,118	9,632	25	yes	yes	EPA Scenario
3F	$P_1 = 145.25$ $P_2 = 955.6$ $n_2 = n_4 = .15$ $K_{11} = K_{12} = 2.8E-2$ $n_{11} = n_{12} = 1E-2$	7,585	7,585	225	yes	no	EPA Scenario
3N	$P_1 = 2.49$ $P_2 = 744.5$ $K_9 = K_{10} = 28.34$ $K_{11} = K_{12} = 1E-4$	29,305	>1E6	0	yes	no	Golder Associates Analysis
60,M2,B1	Base Case Scenario	10,267.5	>1E6	13	yes	no	--
2M,20,6T	$n_{11} = n_{12} = 1E-2$	26,076	134,000	13	yes	no	--
8Y	$n_2 = n_4 = 0.1$	174,172	>1E6	39	no	no	Lower range of U. Aq. n.
8S	$n_9 = n_{10} = 0.01$	13,124	>1E6	39	no	no	Low n for shaft
8R	$n_9 = n_{10} = 1.0$	295,658	>1E6	39	no	no	Darcy velocity in shaft
8Z	$n_2 = n_4 = .30$	379,221	>1E6	39	no	no	High n for U. Aquifer
7R	$K_9 = K_{10} = 2.38E-8$	349,905	350,000	100	no	no	Lowest K for shaft
7D	$K_{11} = K_{12} = 1E-7$	80,137	>1E6	0	no	no	Lowest K for host basalt flow down leg 9
8A	$K_{11} - K_{12} = 1.0$	31,760	34,675	200	no	yes - Tc99	Unreasonable K for basalt; flow down shaft
8J	$K_{11} = K_{12} = 1.0$ $n_{11} = n_{12} = 1E-4$	17,855	17,960	191	no	yes	Lowest for basalt
8E	$K_{11} = K_{12} = 1.0$ $n_{11} = n_{12} = 1.1E-3$	93,787	94,054	191	no	no	Flow down shaft, low basalt n, high
8N	$K_{11} = K_{12} = 1.0$ $n_9 = n_{10} = 0.01$	34,575	34,670	191	no	yes	Low salt n, flow down leg 10
9K	$f_p: 13-1-3-4$	26,076	28,000	13	yes	no	Altered flow path base case
7S	$n_{11} = n_{12} = 1E-1$ $f_p: 13-10-3-4$	81,741	87,964	39	yes	no	v. high basalt porosity
7O	$n_{11} = n_{12} = 1E-2$ $f_p: 13-10-3-4$	81,741	87,964	39	yes	no	High basalt n
7I	$K_9 = K_{10} = 100$ $f_p: 13-10-3-4$	158,097	167,068	57	yes	no	v. high shaft K
7H	$K_9 = K_{10} = 20$ $f_p: 13-10-3-4$	142,193	153,751	55	yes	no	v. high shaft K
7L	$K_{11} = K_{12} = 1E-7$	80,042	89,959	0	yes	no	v. low basalt K flow down leg 9
7E	$n_9 = n_{10} = 0.01$	13,124	19,324	39	yes	no	v. low shaft $n_x$

Table 8 | INPUT PARAMETERS AND MINIMUM GROUNDWATER TRAVEL TIMES (CONTINUED).

7B	$n_9 = n_{10} = 1.0$	295,658	302,000	33	yes	no	v. low shaft $n_x$
K8	$n_9 = n_{10} = 0.01$ $K_9 = K_{10} = 100.0$ $K_{11} = K_{12} = 1E-7$ $f_p = 13 \cdot 10^{-3-4}$	12,855	22,071	0	yes	no	v. high shaft K v. low basalt K
LG	$n_9 = n_{10} = 0.01$ $K_9 = 2.0$ $K_{10} = 100.0$ $K_{11} = K_{12} = 1E-7$ $f_p = 13 \cdot 10^{-3-4}$	12,956	22,680	0	yes	no	failed shaft - v. high K, v. low K basalt, low n for shaft

$f_p =$  flow path

Table 9. Solubility Limits Enforced in Borehole/Shaft Seal Failure Sensitivity Analysis

<u>Isotope</u>	<u>Solubility (gm/gm)</u>	<u>Source</u>
C14	10.0*	EPA 520/3-80-006
Ni59	10.0*	Infinite Solubility
Sr90	9.0E-5	Geotrans Parameter Listing
Zr93	2.34E-11	Geotrans Parameter Listing
Tc99	7.8E-10	Mean Value used in Sensitivity Analysis, M.J. Wise
Sn126	1.26E-10	Geotrans Parameter Listing
U234	2.34E-4	Geotrans Parameter Listing
Pu239	2.39E-9	Geotrans Parameter Listing
Pu240	2.40E-9	Geotrans Parameter Listing

\* indicates that the actual solubility is unknown and so the species has been assumed to be infinitely soluble (i.e. 10 grams solute/ gram solution).

#### References

##### Geotrans Parameter Listing:

Mercer, J.W., Thomas, S.D., and Ross, B. Parameters and Variables Appearing in Repository Siting Models, Geotrans, Inc., 1982.

##### EPA 520/3-80-006:

Smith, C.B., Egan, D.J., Williams, W.A., Gruhlke, J.M., Hung, C., and Serini, B.L. Population Risks from Disposal of High-Level Radioactive Wastes in Geologic Repositories (Draft), U.S. EPA 520/3-80-006, 1981.

##### Sensitivity Analysis:

NRC in-house sensitivity analysis being prepared by Performance Assessment Staff in High-Level Waste Management Licensing Branch; M.J. Wise, principal investigator.

Table 10. Distribution Coefficients and Retardation Factors in the Borehole/Shaft Seal Failure Sensitivity Analysis

A. Host Basalt Flow Path (13-12-7-14-4)

DISTRIBUTION COEFFICIENTS BY LEG AND BY ISOTOPE

	C14	NI59	SR90	ZR93	TC99	SN126	U234	PU239	PU240
LEG13	0.	.34000E+01	.34000E+01	.34000E+01	0.	.34000E+01	.12000E+00	.44000E+00	.44000E+00
LEG12	0.	.34000E+01	.34000E+01	.34000E+01	0.	.34000E+01	.12000E+00	.44000E+00	.44000E+00
LEG 7	0.	.18000E+00	0.	.18000E+00	0.	.18000E+00	.12000E+00	.44000E+00	.44000E+00
LEG14	0.	.18000E+00	0.	.18000E+00	0.	.18000E+00	.12000E+00	.44000E+00	.44000E+00
LEG 4	0.	.18000E+00	0.	.18000E+00	0.	.18000E+00	.12000E+00	.44000E+00	.44000E+00

RETARDATION FACTORS BY LEG AND BY ISOTOPE

	C14	NI59	SR90	ZR93	TC99	SN126	U234	PU239	PU240
LEG13	.10000E+01	.57900E+03	.57900E+03	.57900E+03	.10000E+01	.57900E+03	.21400E+02	.75800E+02	.75800E+02
LEG12	.10000E+01	.52488E+06	.52488E+06	.52488E+06	.10000E+01	.52488E+06	.18526E+05	.67926E+05	.67926E+05
LEG 7	.10000E+01	.95595E+05	.10000E+01	.95595E+05	.10000E+01	.95595E+05	.63731E+05	.23308E+06	.23308E+06
LEG14	.10000E+01	.95595E+05	.10000E+01	.95595E+05	.10000E+01	.95595E+05	.63731E+05	.23308E+06	.23308E+06
LEG 4	.10000E+01	.30304E+04	.10000E+01	.30304E+04	.10000E+01	.30304E+04	.20206E+04	.74062E+04	.74062E+04

B. Failed Shaft Flow Path (13-10-3-4)

DISTRIBUTION COEFFICIENTS BY LEG AND BY ISOTOPE

	C14	NI59	SR90	ZR93	TC99	SN126	U234	PU239	PU240
LEG13	0.	.34000E+01	.34000E+01	.34000E+01	0.	.34000E+01	.12000E+00	.44000E+00	.44000E+00
LEG10	.10000E+05	0.	.10000E+01	.14995E+03	0.	0.	.49500E+01	.14995E+03	.14995E+03
LEG 3	0.	.18000E+00	0.	.18000E+00	0.	.18000E+00	.12000E+00	.44000E+00	.44000E+00
LEG 4	0.	.18000E+00	0.	.18000E+00	0.	.18000E+00	.12000E+00	.44000E+00	.44000E+00

RETARDATION FACTORS BY LEG AND BY ISOTOPE

	C14	NI59	SR90	ZR93	TC99	SN126	U234	PU239	PU240
LEG13	.10000E+01	.57900E+03	.57900E+03	.57900E+03	.10000E+01	.57900E+03	.21400E+02	.75800E+02	.75800E+02
LEG10	.10000E+01								
LEG 3	.10000E+01	.30600E+09	.10000E+01	.30600E+09	.10000E+01	.30600E+09	.20400E+09	.74800E+09	.74800E+09
LEG 4	.10000E+01	.30304E+04	.10000E+01	.30304E+04	.10000E+01	.30304E+04	.20206E+04	.74062E+04	.74062E+04

(Input parameter outputs from selected runs using NWFT/DVM).

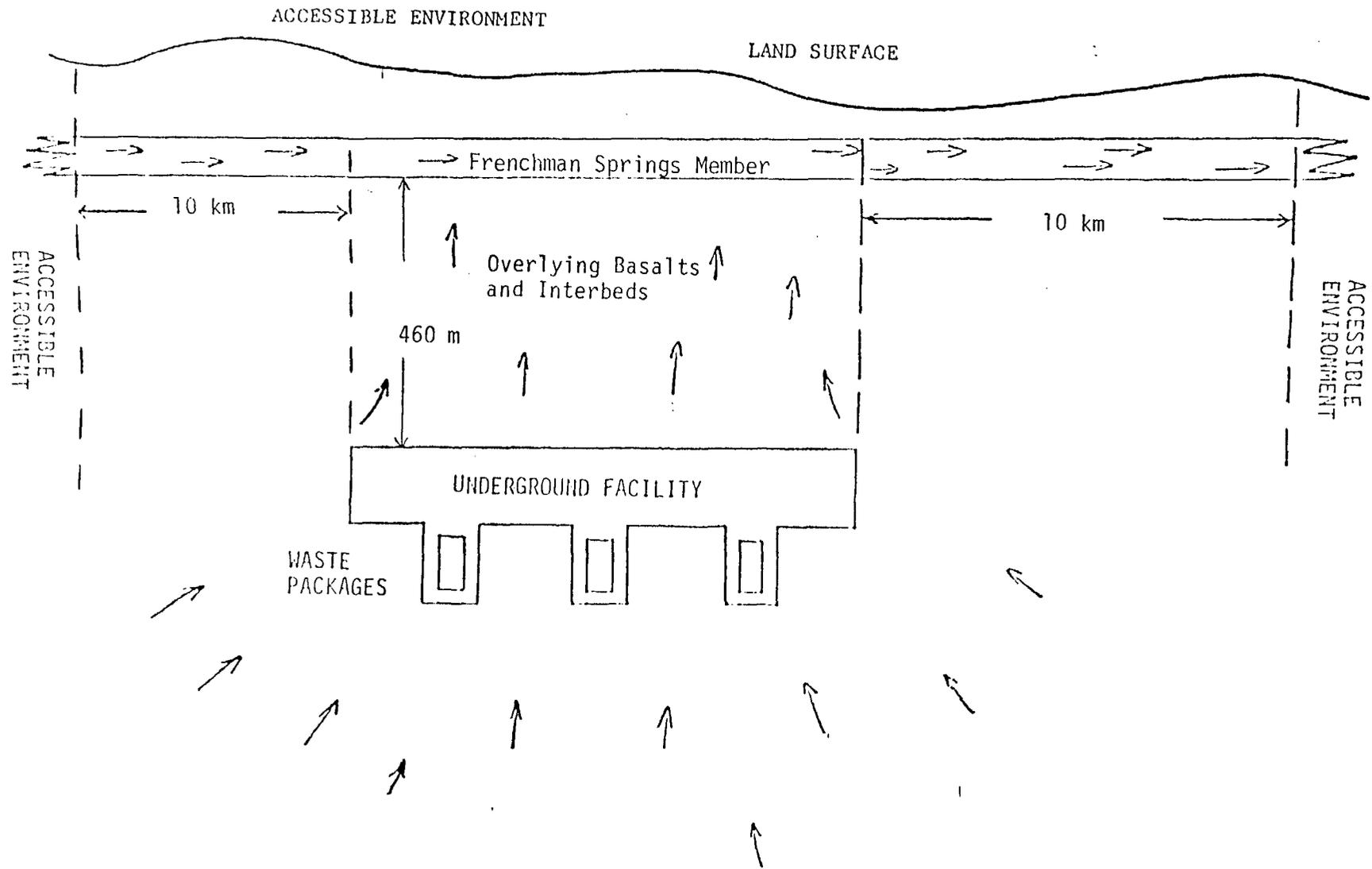


FIGURE 1 - DIAGRAM OF ENGINEERED BARRIER SYSTEM AND GEOLOGIC SETTING.

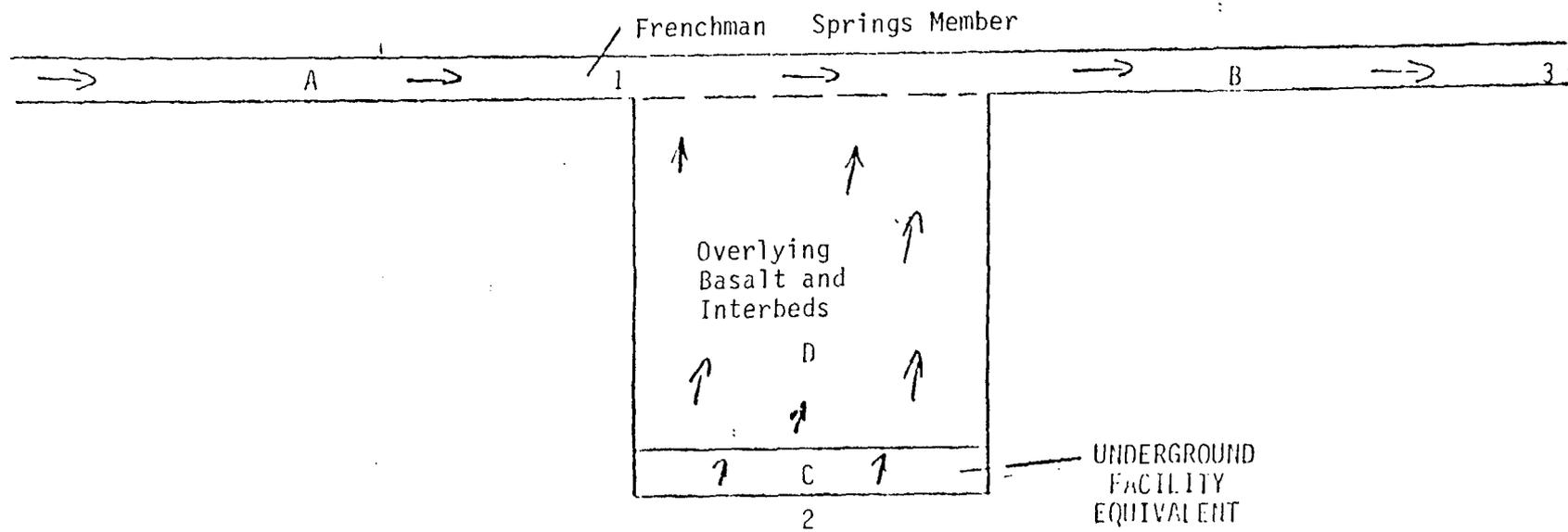


FIGURE 2 - UNIDIRECTIONAL FLOW MODEL CORRESPONDING TO FIGURE 1.

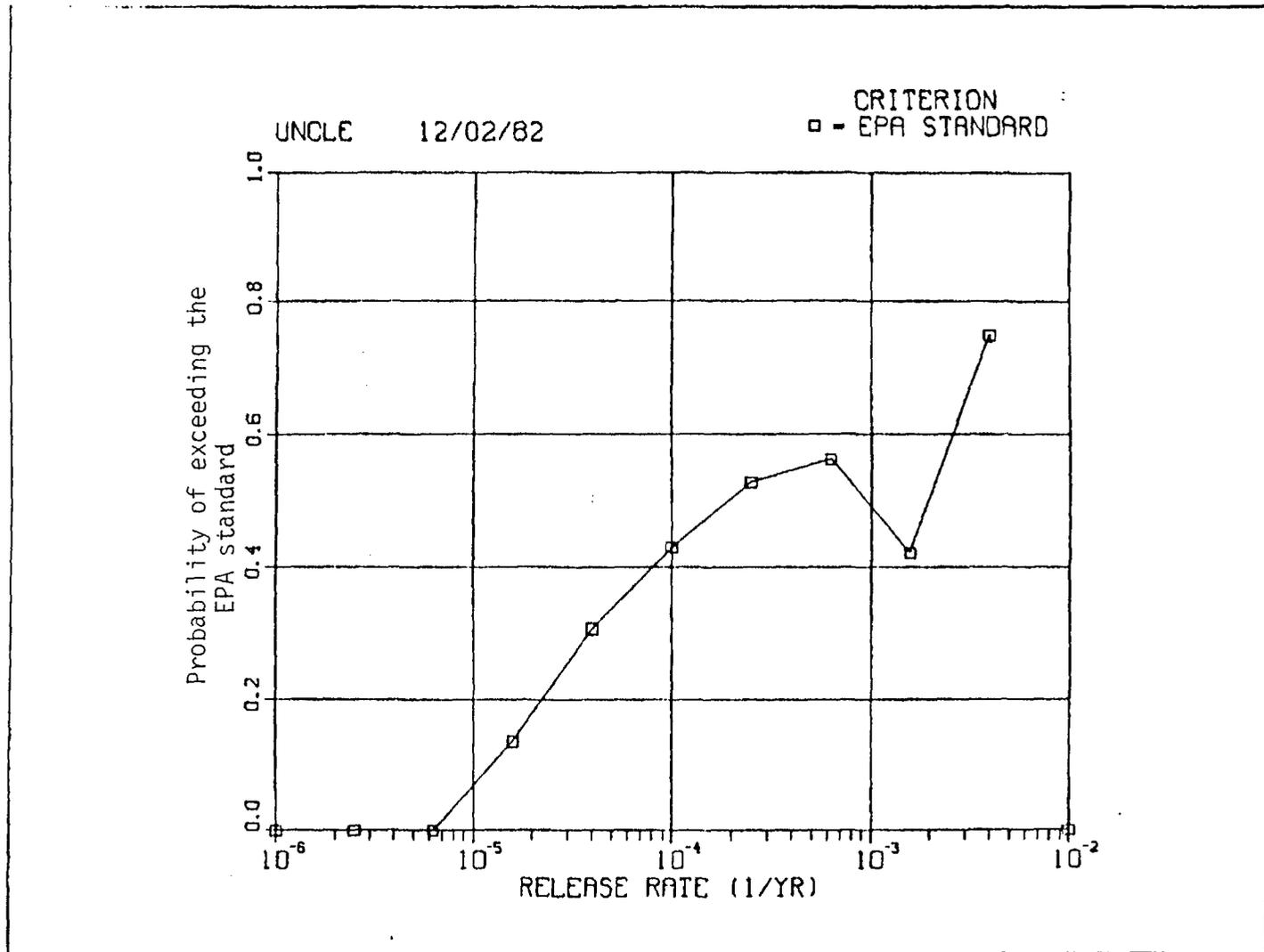
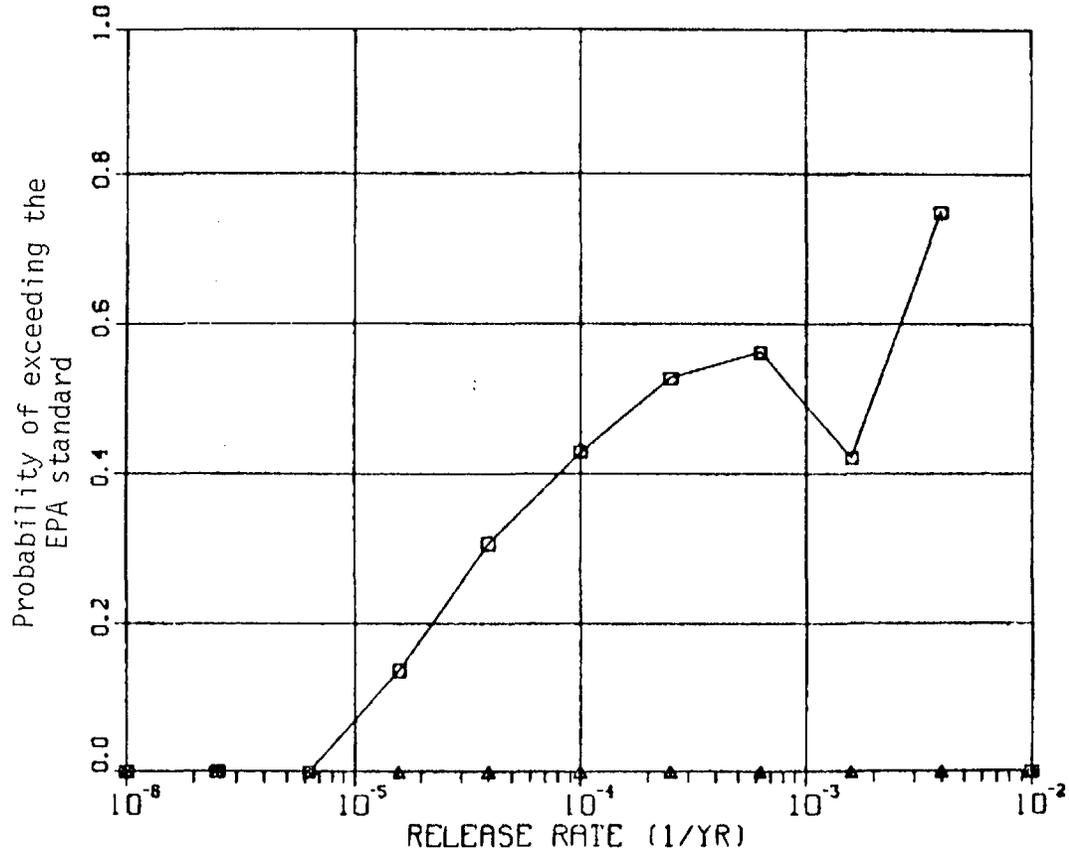


Figure 3.

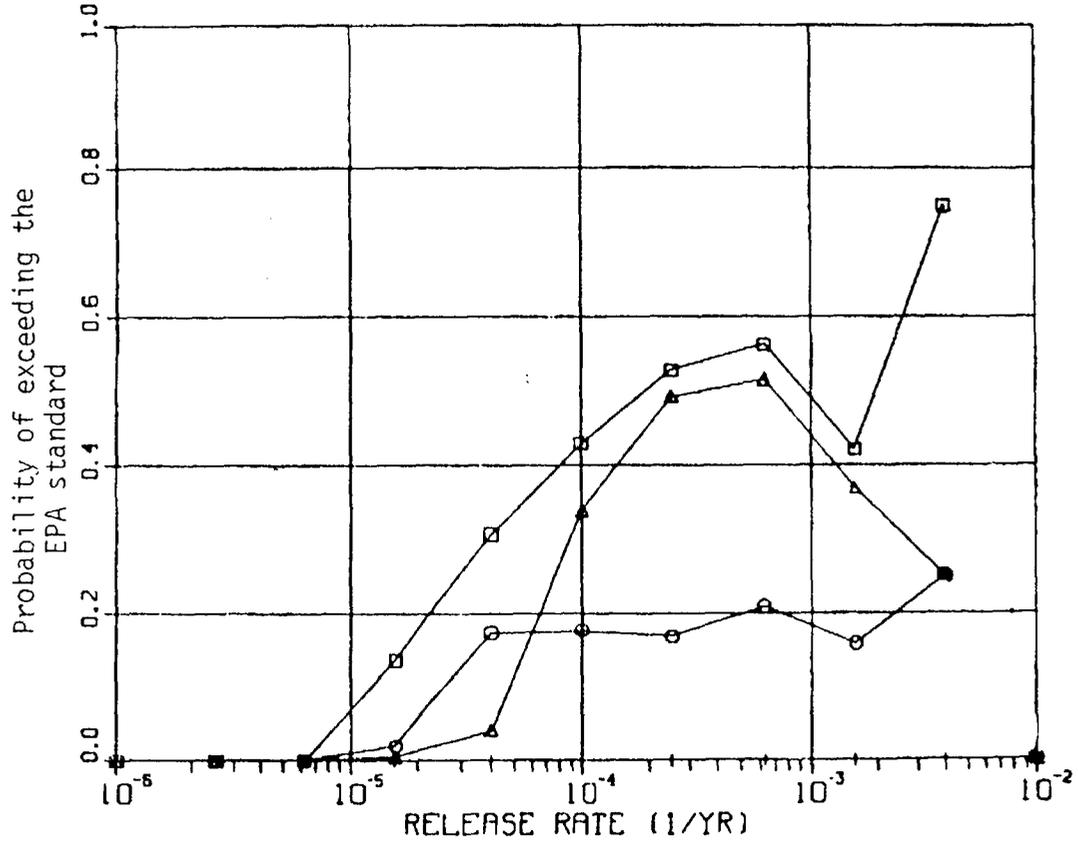
UNCLE 12/03/82

CRITERION  
□ - EPA STANDARD  
○ - UNRETARDED FP  
△ - RETARDED FP  
+ - ACTINIDES



UNCLE 12/03/82

CRITERION  
□ - EPA STANDARD  
○ - TC99  
△ - C14  
+ - I129



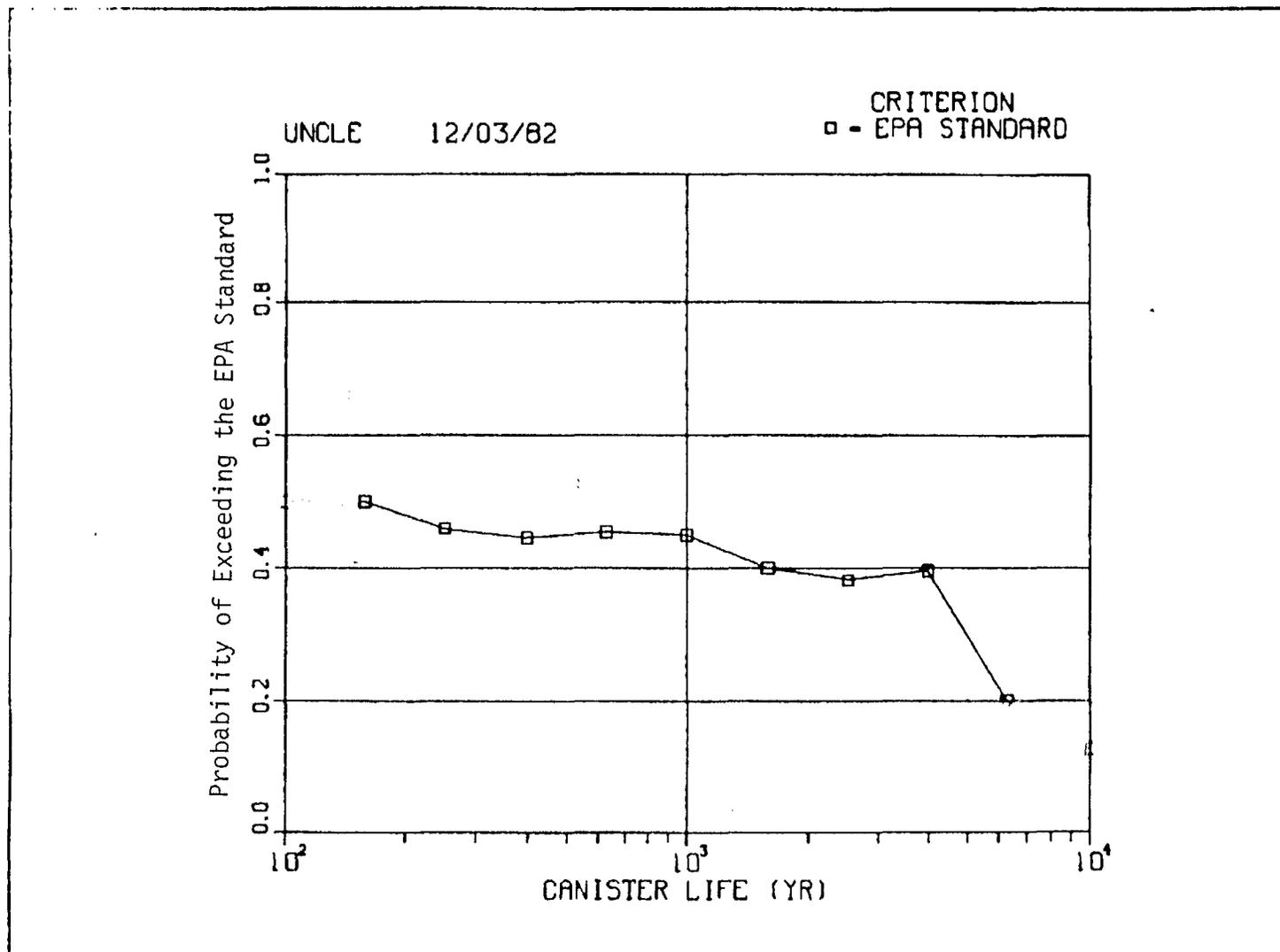


FIGURE 6

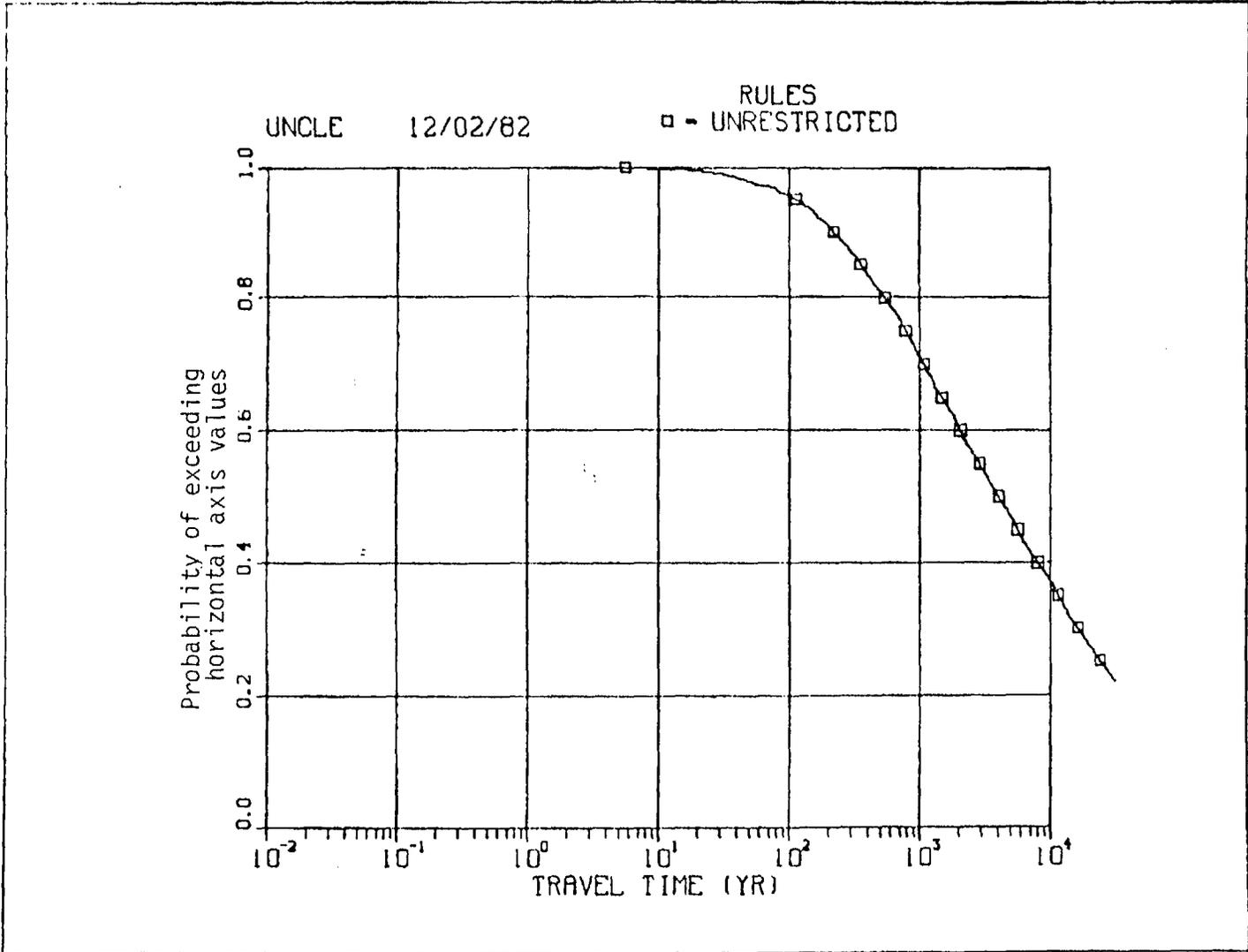
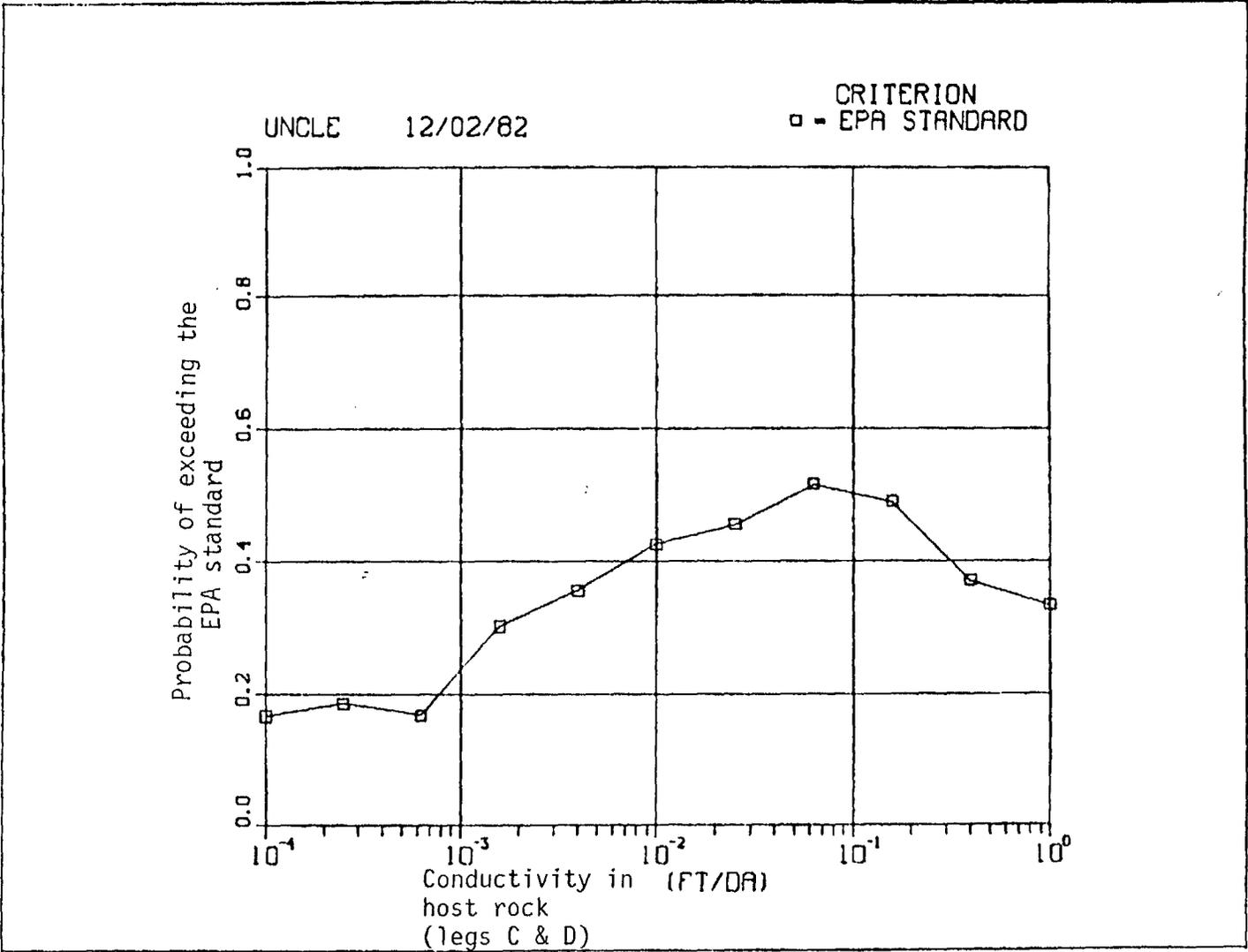
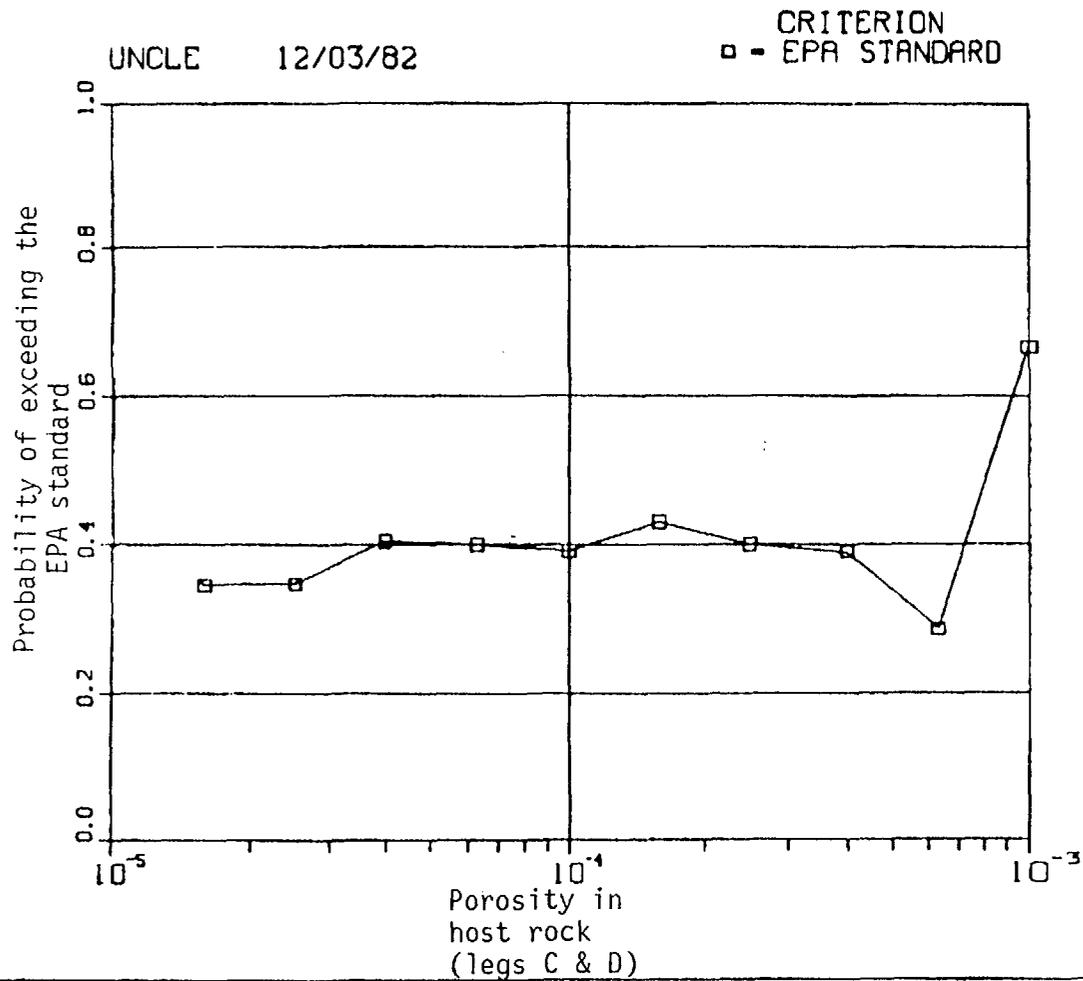
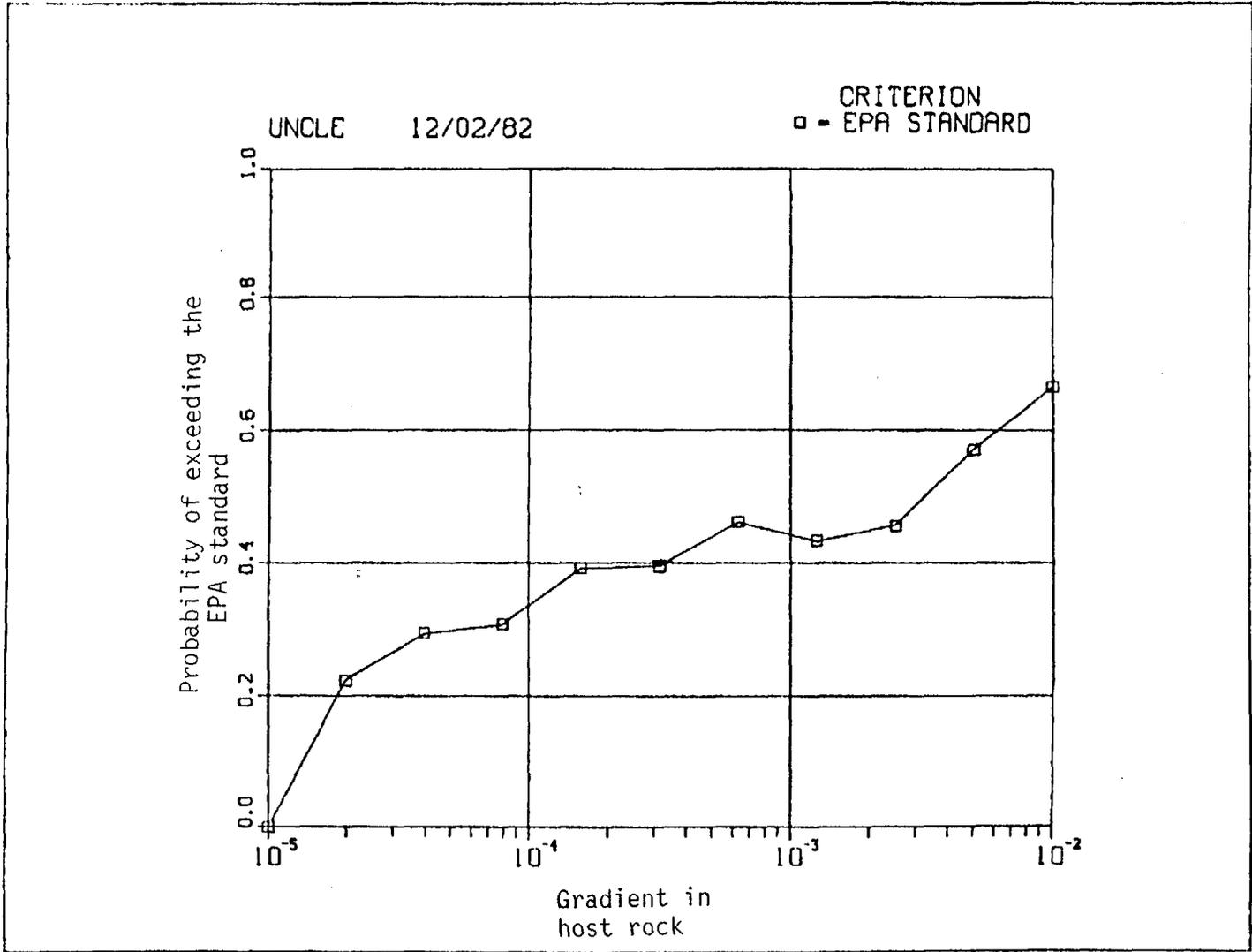


Figure 7







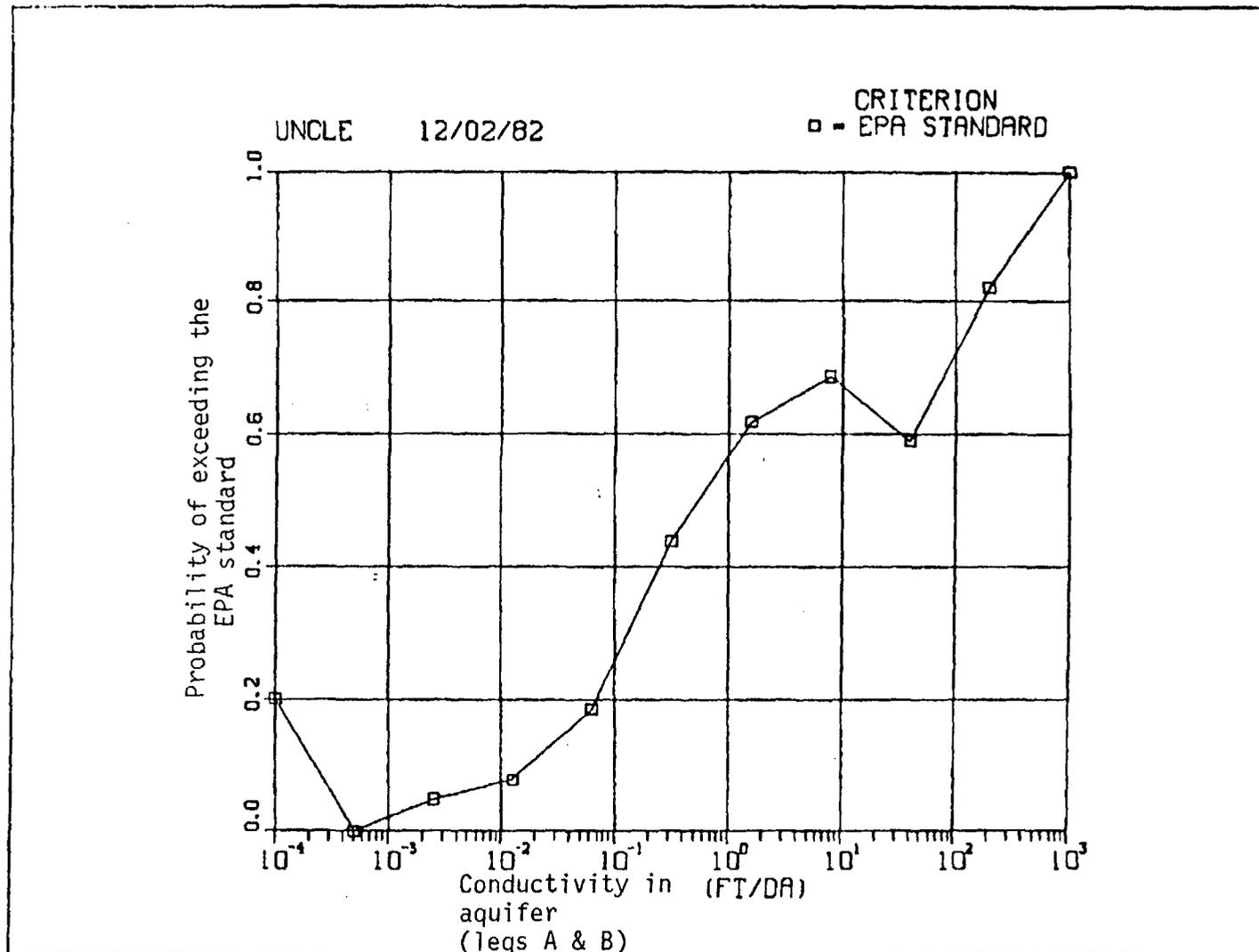


Figure 11

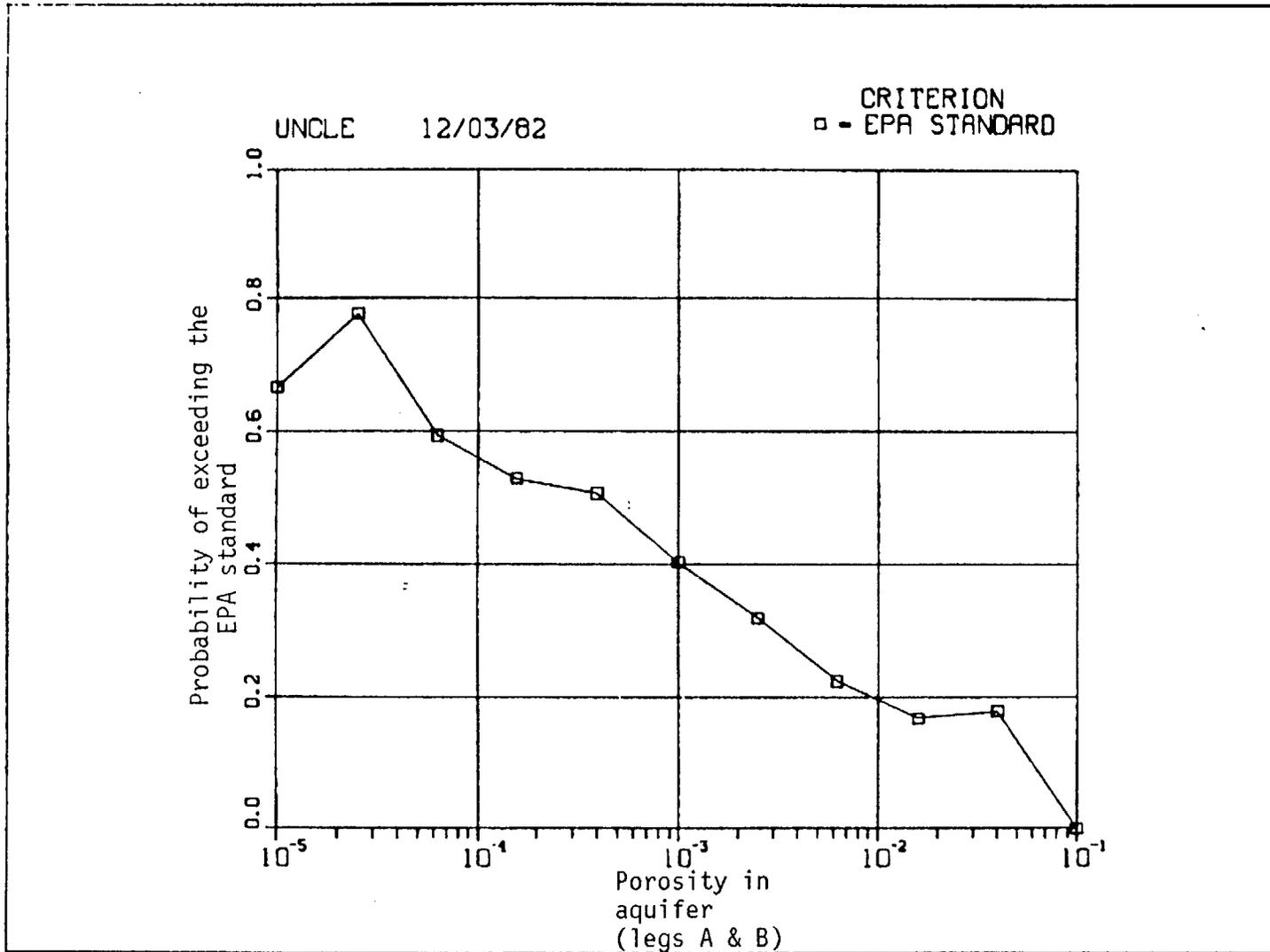


Figure 12.

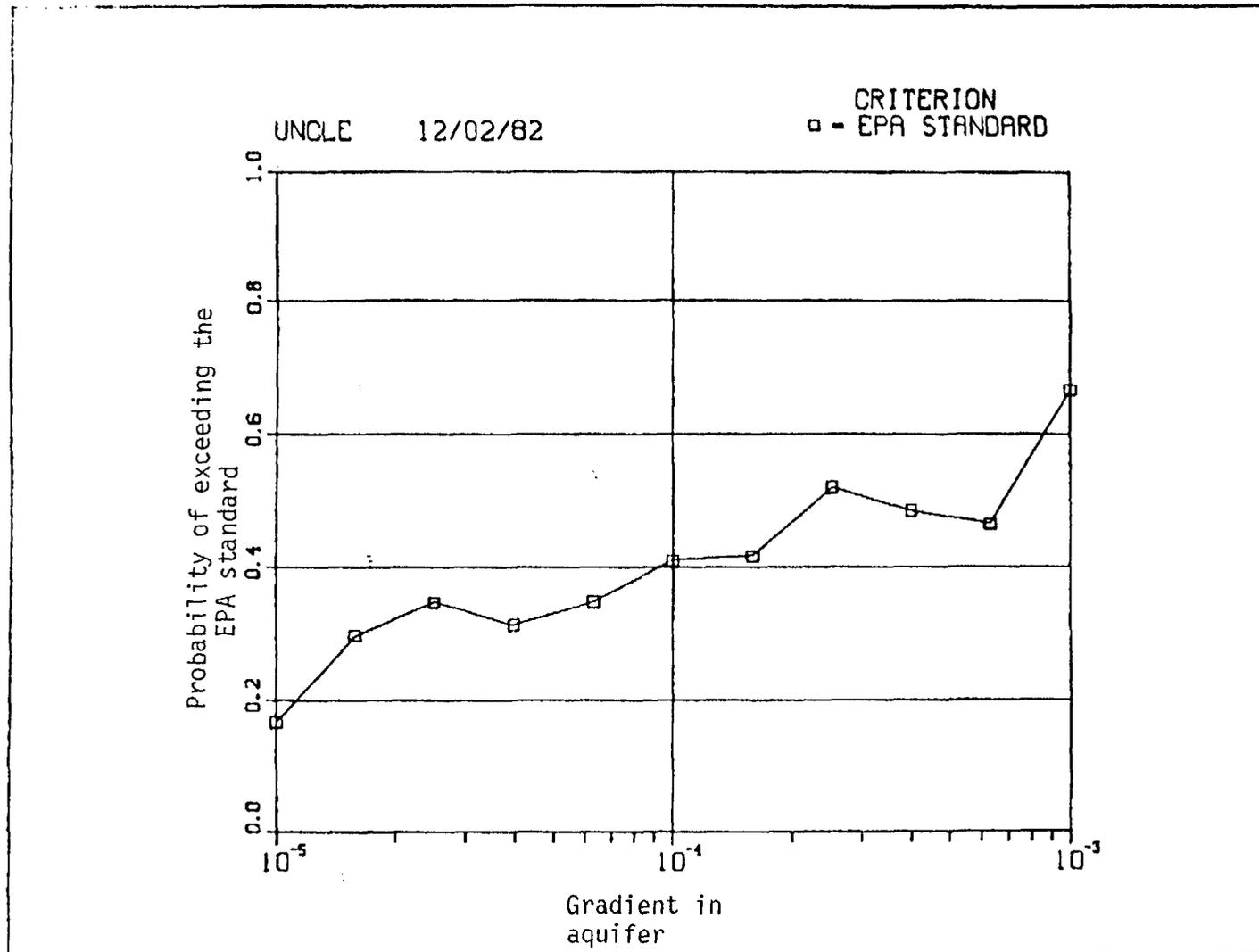


Figure 13.

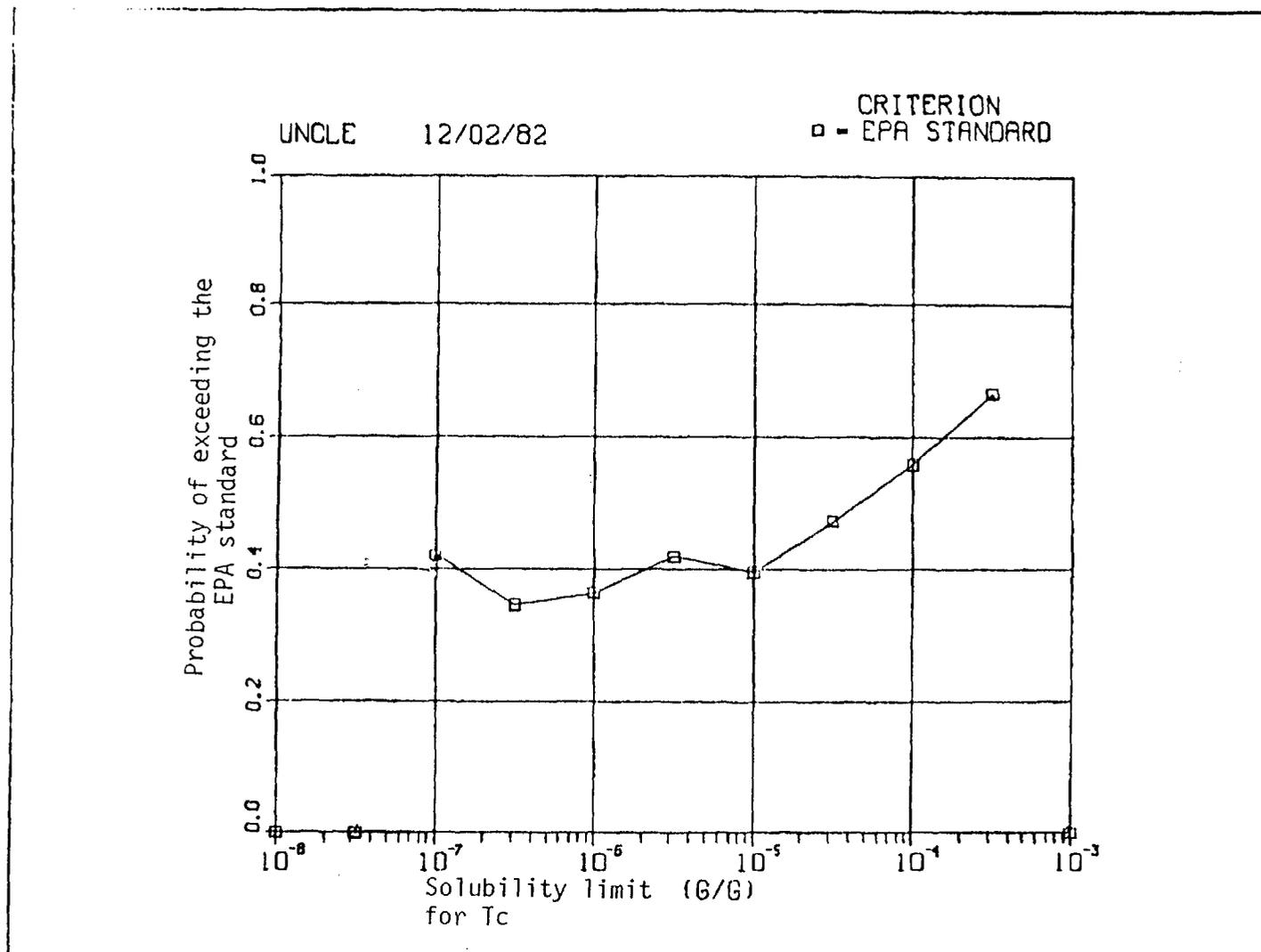


Figure 14.

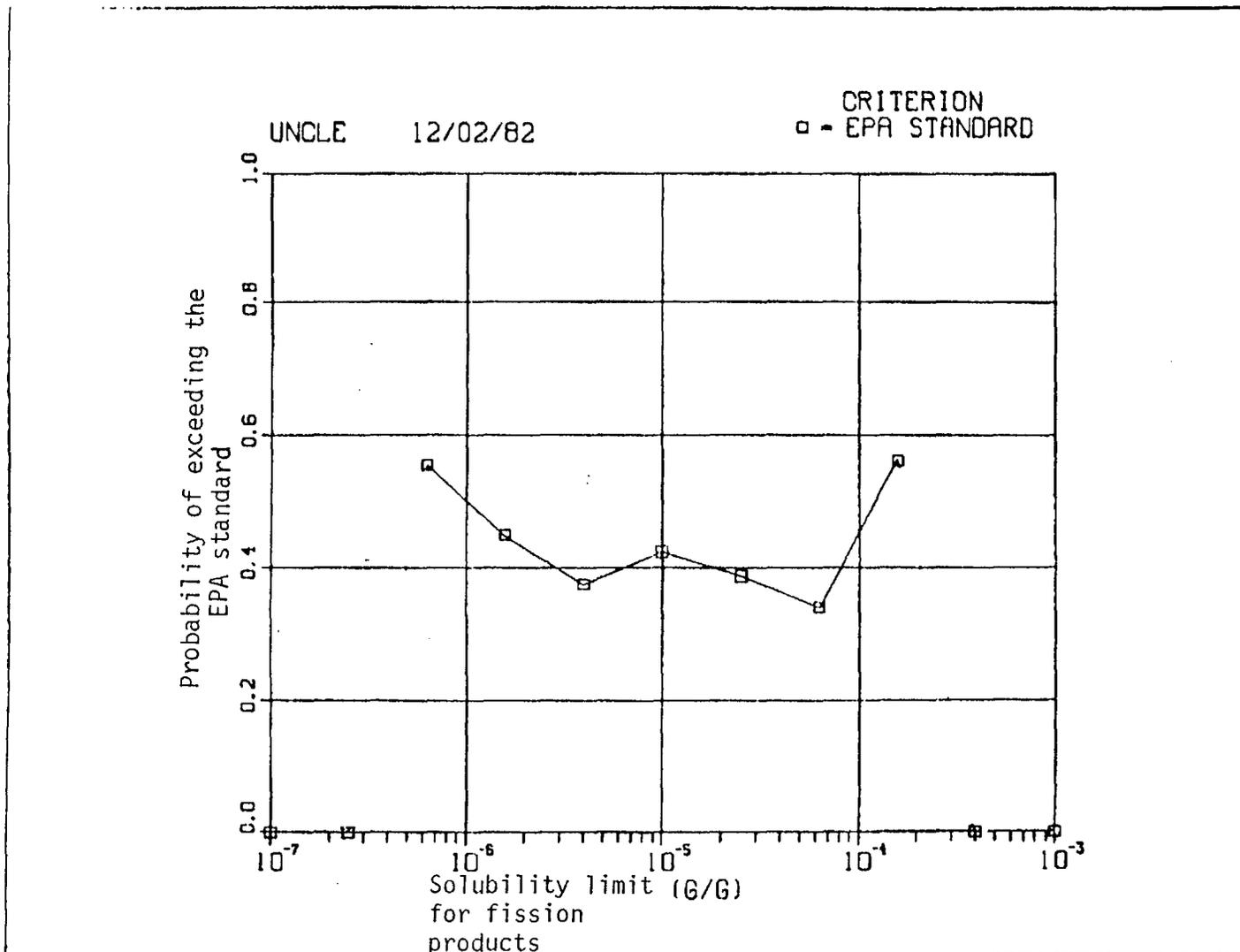


Figure 15.

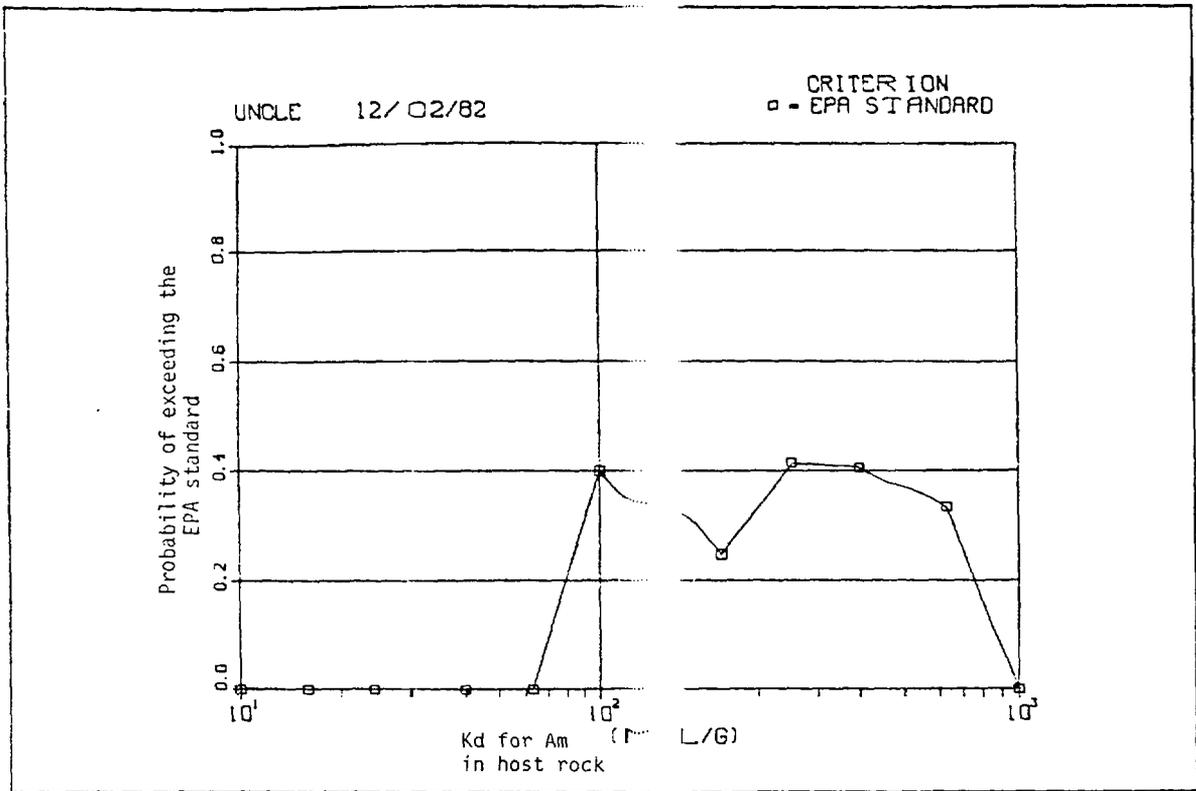


Figure 17a

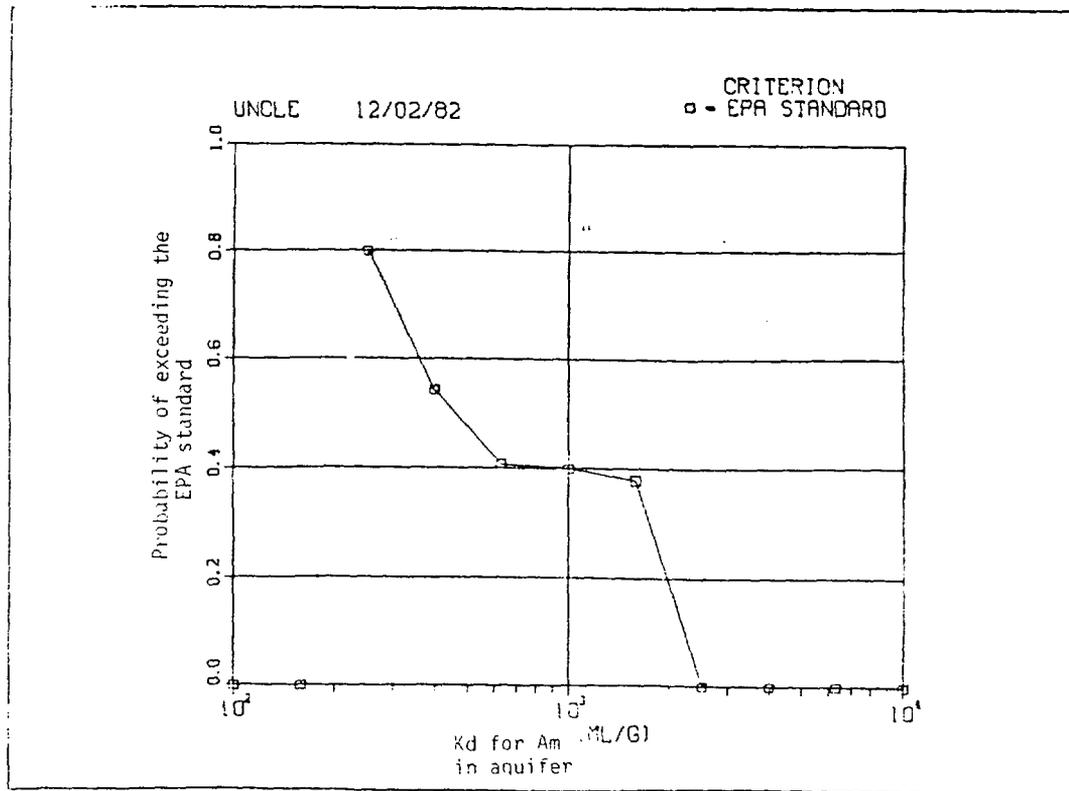


Figure 17b

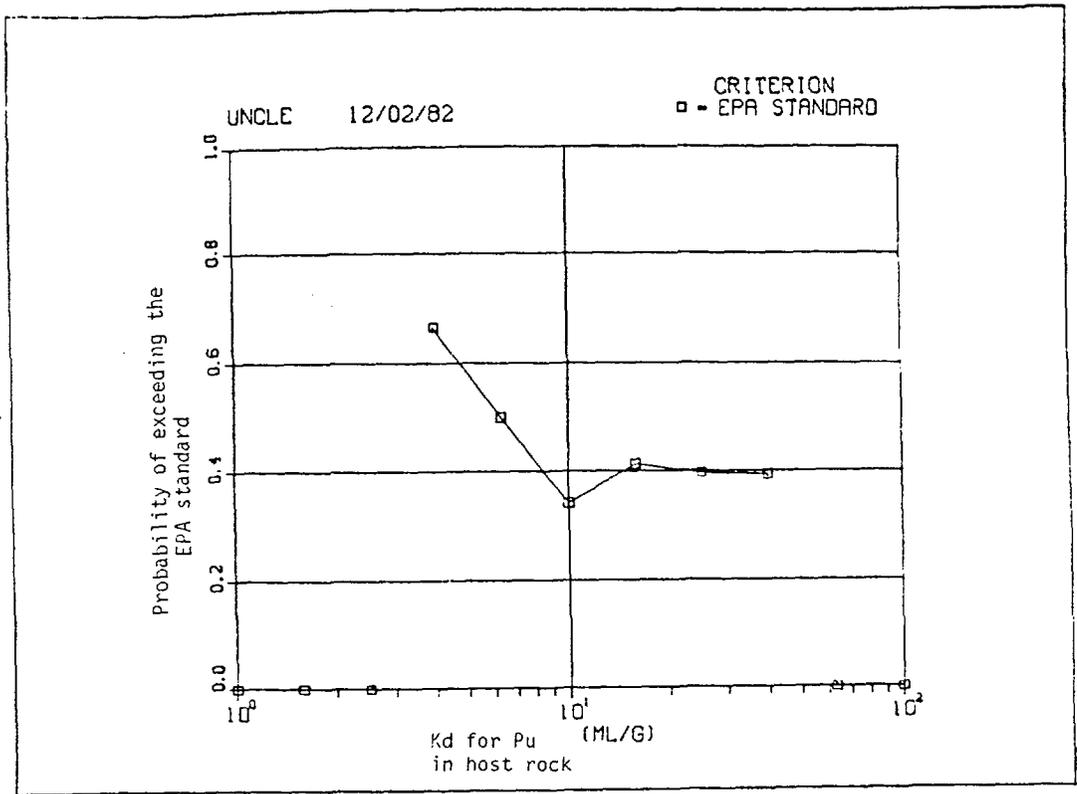


Figure 17a.

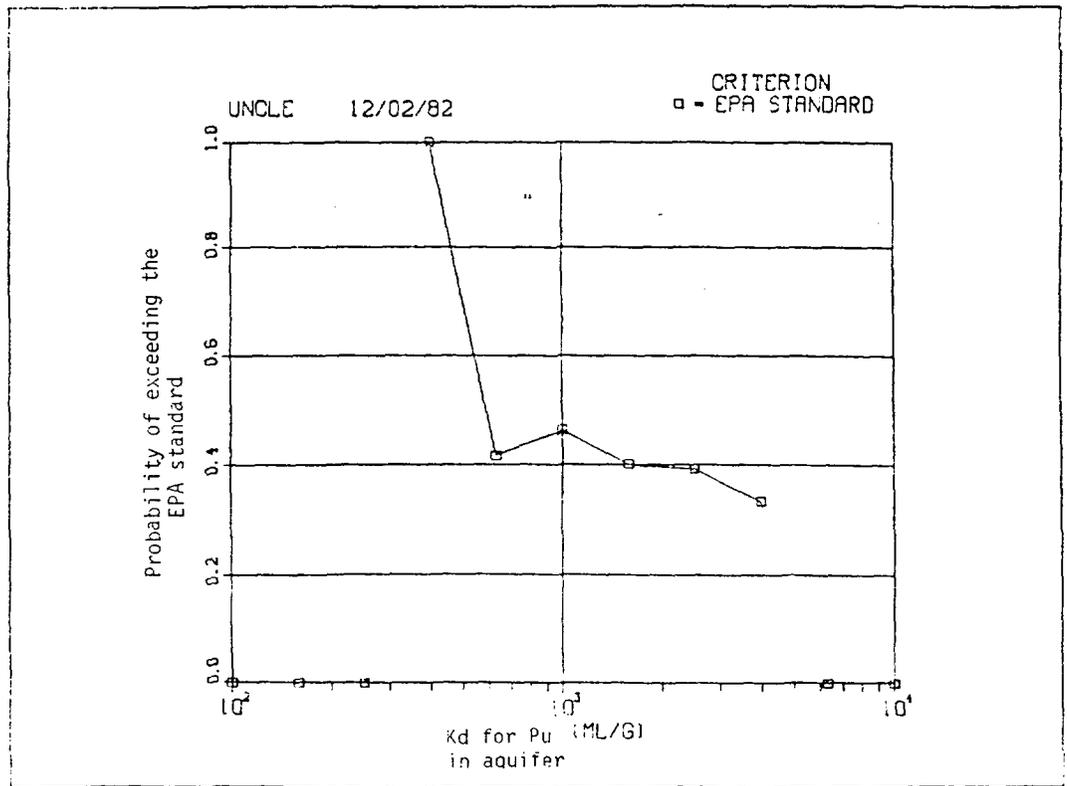


Figure 17b.

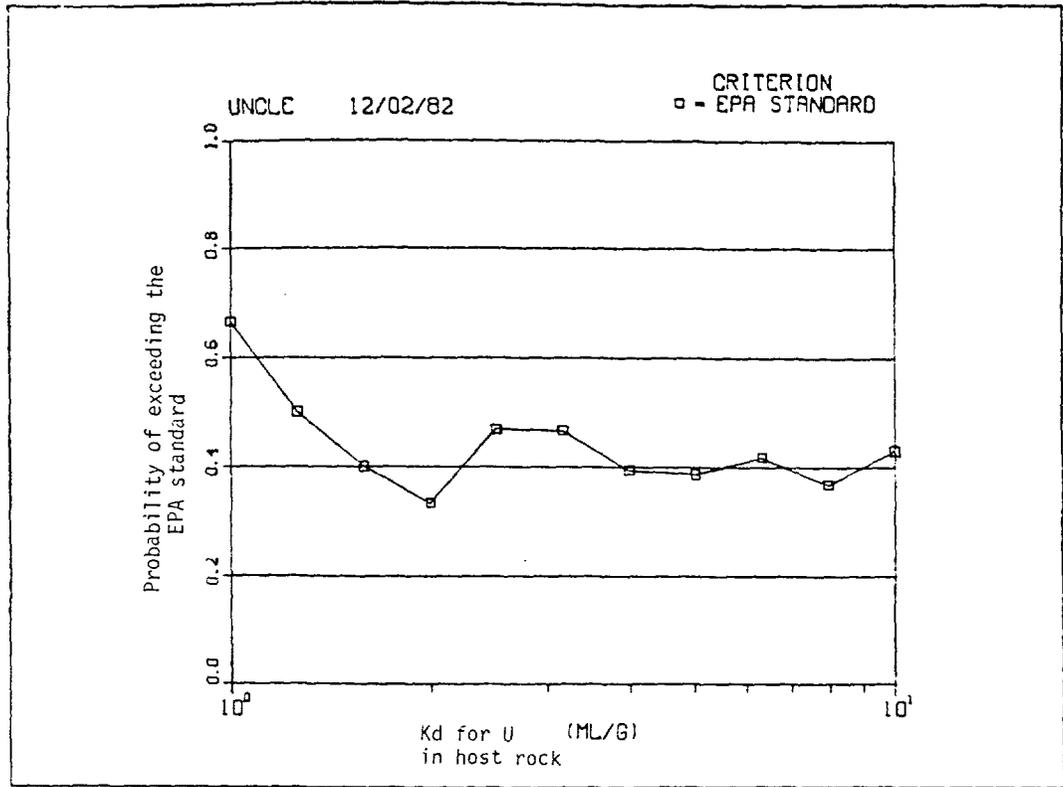


Figure 18a.

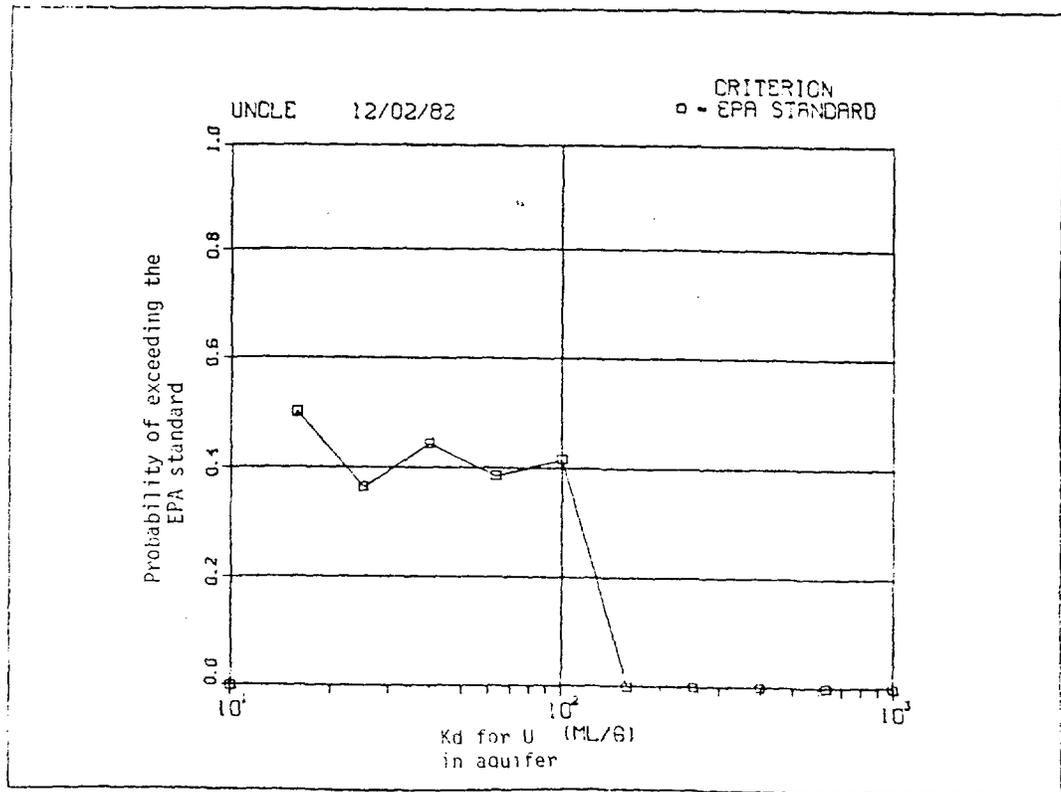


Figure 18b.

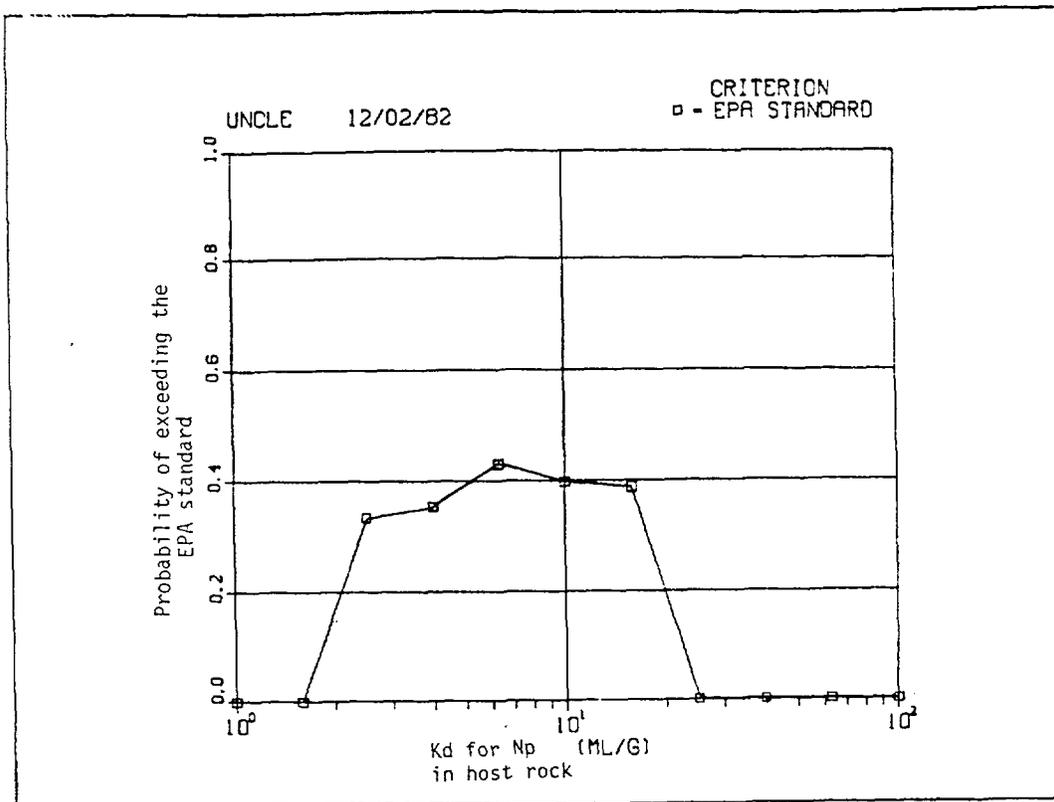


Figure 19a.

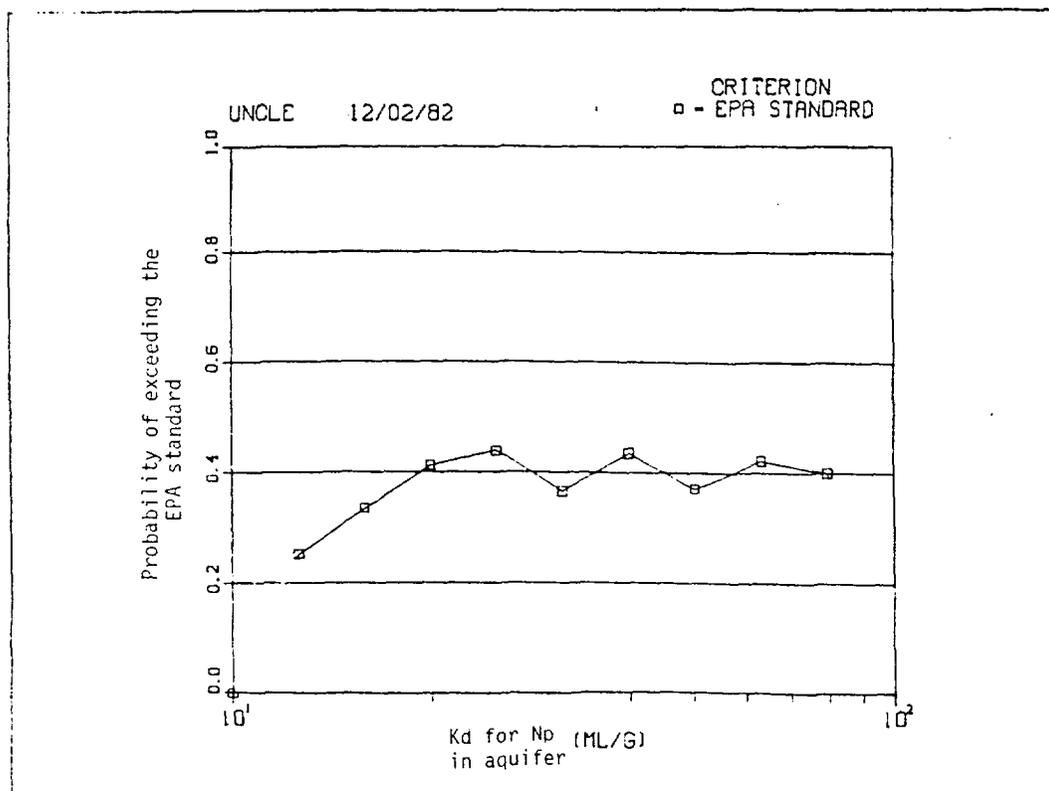


Figure 19b.

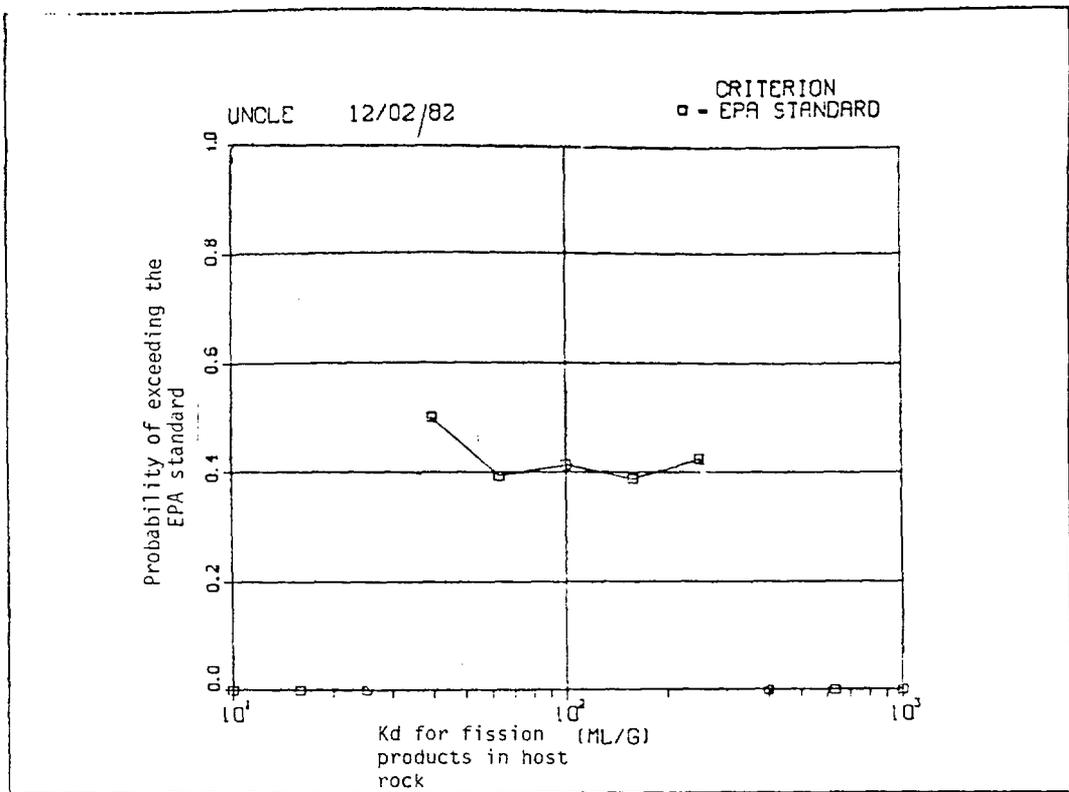


Figure 20a.

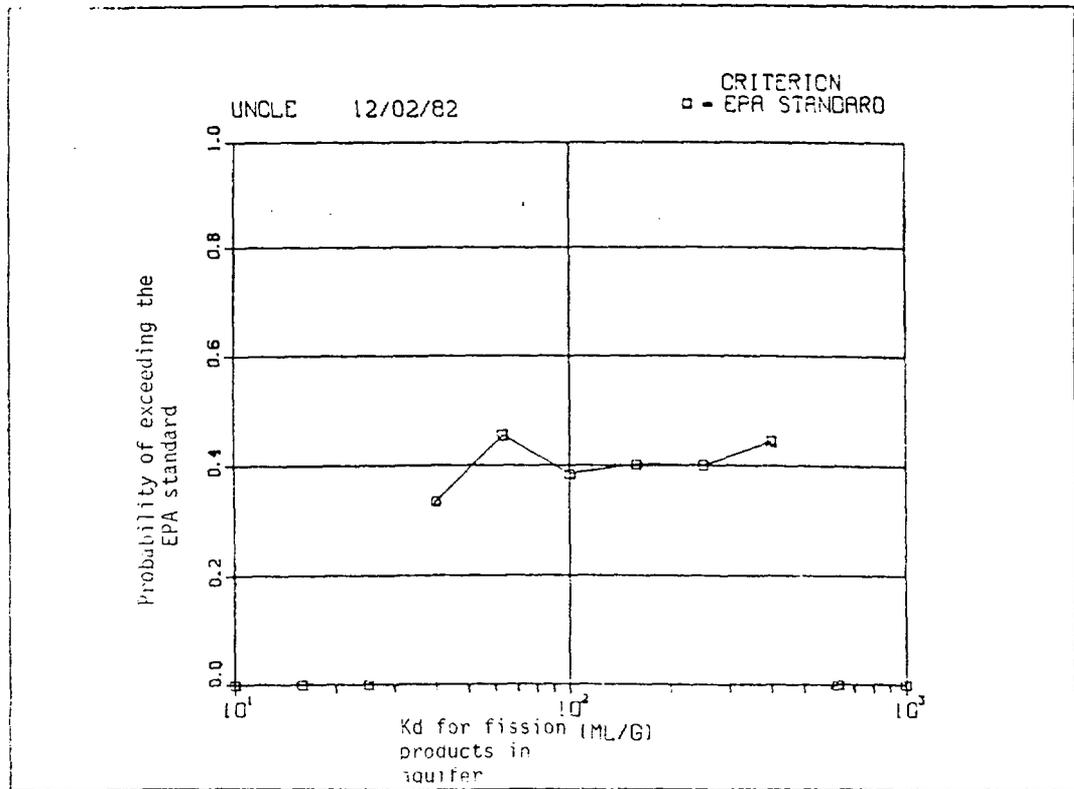


Figure 20b.

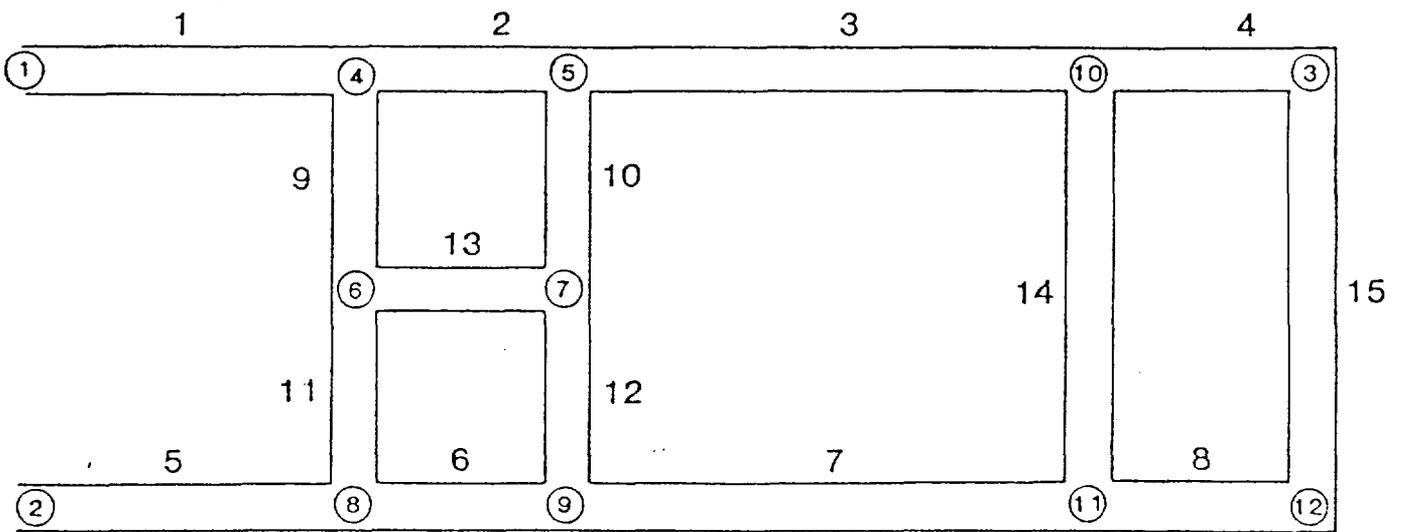


Figure 21. Basic Flow Network of NWFT/DVM (Campbell, Longsine, and Cranwell, 1981).

NWFT/DVM DATA SHEET

Row Number: WEBER MW2 / 11/22/82 (DATE)

LEG NUMBER	HYDRAULIC CONDUCTIVITY (FT/DAY)	X-SECTIONAL AREA (FT <sup>2</sup> )	LENGTH (FT)	PERMEABILITY (FRACITM)	BRINE C.	MATERIAL	COMMENT
1	1E8	1.0	100.0	1E-4	0.0	PIPE	
2	0.19	5.9E6	620.0	0.01	0.0	Upper Aquifer	
3	1E8	1.0	100.0	1E-4	0.0	PIPE	
4	0.19	5.9E6	3.28E4	0.01	0.0	Upper Aquifer	
5	1E8	1.0	100.0	3.2E-4	0.0	PIPE	
6	1E-6	5.9E6	620.0	1E-5	0.0	CUTOFF PIPE	
7	1E8	1.0	100.0	3.2E-4	0.0	PIPE	
8	1E-6	5.9E6	3.28E4	1E-5	0.0	CUTOFF PIPE	
9	2.0	300.0	1500.0	0.25	0.0	FAILED SHAFT	
10	2.0	300.0	1500.0	0.25	0.0	FAILED SHAFT	
11	1E-3	8.EG	200.0	3.2E-4	0.0	LOWER BASALT	
12	1E-3	8.EG	1500.0	3.2E-4	0.0	UPPER BASALT	
13	0.1	104.0	620.0	0.5	0.0	REPOSITORY	
14	1E8	1.0	100.0	3.2E-4	0.0	CUTOFF PIPE	
15	1E-6	5.9E6	100.0	1E-5	0.0	CUTOFF PIPE	

PRESSURES:  $P_1 = 7.11$  psi  $P_2 = 748.11$  psi  $P_3 = 0.0$  psi

$D_x = 100.0$  feet  $D_T = 50.0$  years  $N_{SB} = 2$

RESULTS:

BASECASE DATA INPUT  
DESCRIBING FLOW NETWORK.

Figure 10. Listing of Input Parameters for the Basecase Scenario.

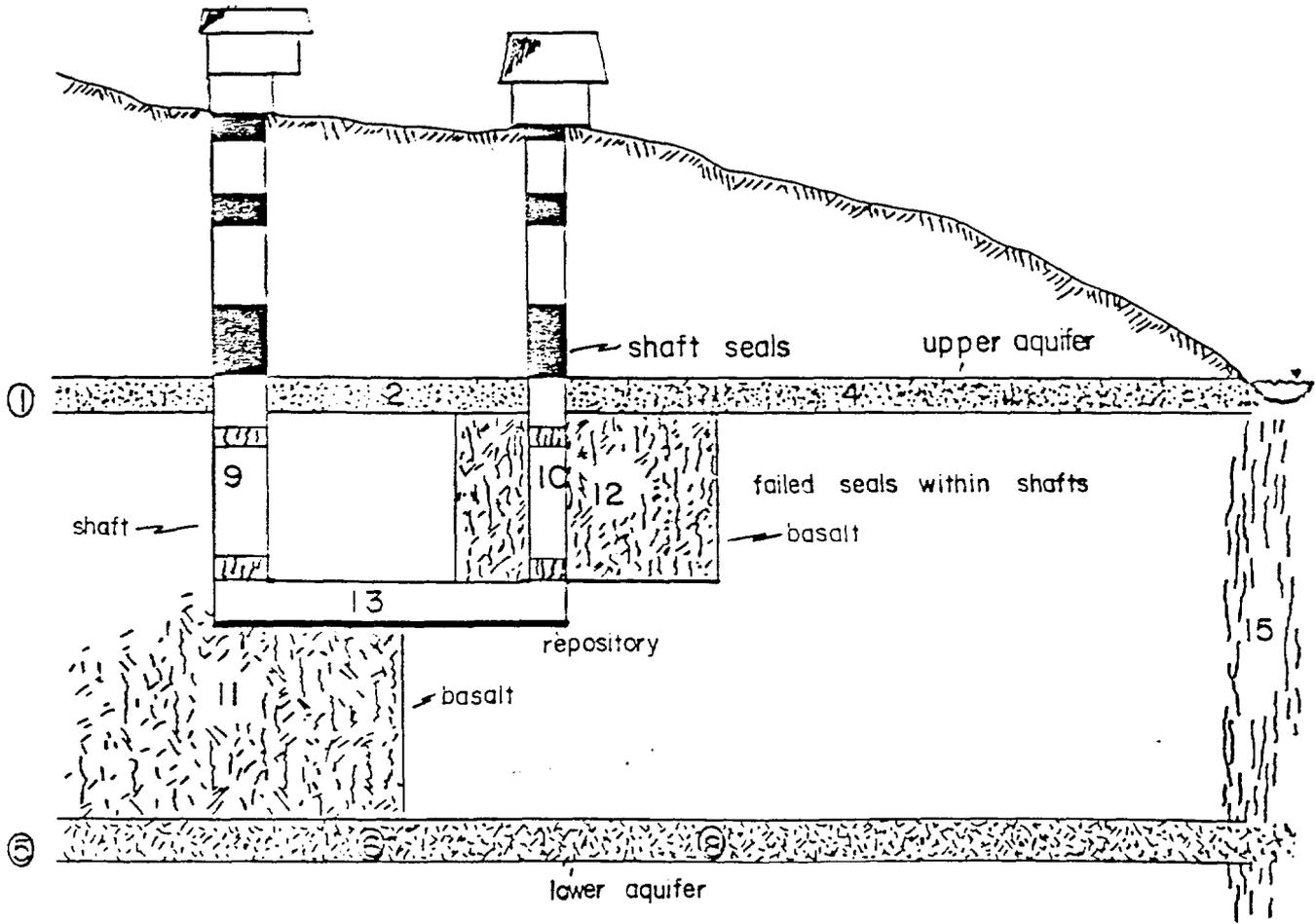


Figure 2.3 Effective Model Network for the Borehole/Shaft Seal Failure Sensitivity Analysis.

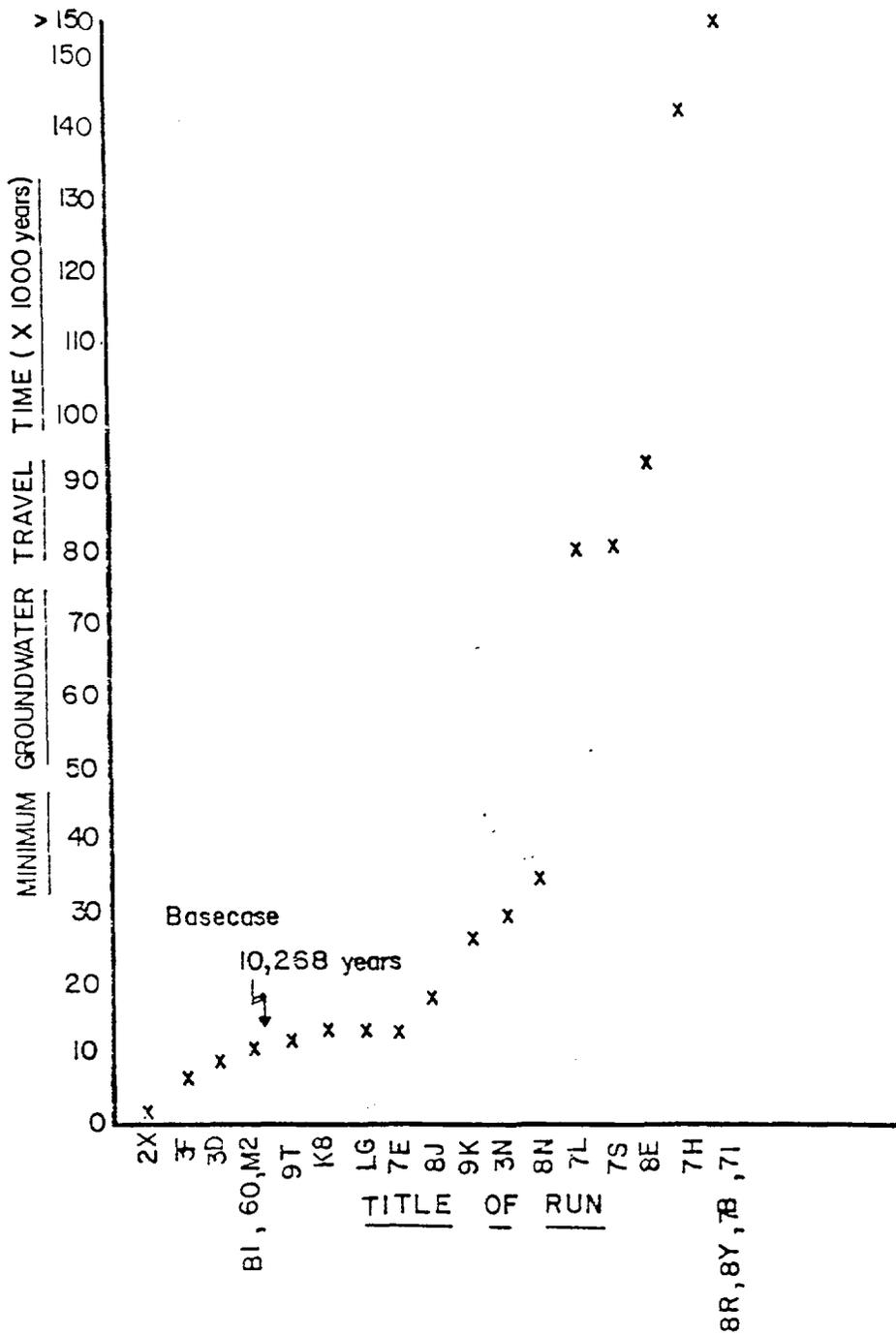


Figure 7 Graph of Minimum Groundwater Travel Times versus Title of Computer Model ( Run Title).

APPENDIX P

FAILURE MODES FOR THE METALLIC WASTE PACKAGE COMPONENT

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## 1 INTRODUCTION AND PURPOSE

Cast steel and cast iron canisters have been identified by BWIP for storage of radioactive waste in a basalt rock repository. Although many studies of container integrity have been made providing satisfactory fracture, corrosion fatigue and uniform corrosion degradation rates (Charlot, Newby 1982, Gause, Newby 1981, Molecke) this appendix reviews these degradation processes in the context of a repository environment and waste package design identified in the BWIP SCR. Its objectives are as followed:

- (a) To address a broad scope of corrosion types and mechanisms for corrosion of waste canisters.
- (b) To conduct a literature survey of both experimental and theoretical work that can provide understanding to model corrosion mechanisms within a basalt repository. Data bases used include the following: Navy studies of brine corrosion; DOE sponsored investigations; microbial corrosion studies; oxide characterization, integrity, and adherence studies; investigations of radiation, heat transfer and hydrogen overpressure effects on iron and steel, and symposia on localized corrosion.
- (c) To identify and discuss probable failure modes and to estimate when failures may occur as a function of canister design.
- (d) To identify crucial uncertainties in our understanding canister lifetime and thus indicate a need for duty to improve this understanding.

## 2 LITERATURE BACKGROUND

### 2.1 Theory

Corrosion is an electrochemical process which oxidizes metals. An electrochemical cell requires a potential (electromotive force) and involves an

oxidation (corrosion) reaction and a reduction reaction. Within this cell, oxidation takes place at the anode and reduction at the cathode. For example:



Electrons flow through the base metal from the anode to the cathode. The circuit is completed by ion migration through solution (or condensed moisture) in contact with the metal surface. Oxygen often facilitates corrosion. Sources of oxygen include  $\text{O}_2$  in air or water and electrochemical breakdown or radiolysis of water. Electrical potential is provided by a differential in almost any parameter of the system, e.g., chemical composition, pH, oxygen concentration, temperature.

Since iron is thermodynamically not favored as an ion in water when oxygen or hydroxide is present, rust is precipitated from solution. "Rust" can take the form of an oxide, magnetite ( $\text{Fe}_3\text{O}_4$ ) or hematite ( $\text{Fe}_2\text{O}_3$ ), a hydroxide, or some other species, including potentially colloidal species in suspension. Thermodynamic equilibria indicate which corrosion products will be stable in a given system. For aqueous systems, Pourbaix diagrams applicable to systems in equilibrium show stable regions at constant temperature and varying potentials (Eh) and pH's. Figures 1 and 2 show corrosion and passivation behavior for a pure iron system. These particular diagrams are an aid in predicting oxide stability, however, their applicability in a repository situation is limited for several reasons. First, Figures 1 and 2 are for a system at  $25^\circ\text{C}$  while repository conditions are calculated to range from  $300^\circ\text{C}$  to  $65^\circ\text{C}$ . Secondly, this is a binary system at equilibrium and unit activity. Repository conditions will have chemical gradients, temperature gradients and stresses as well as the added components of salts and dissolved hydrogen (due to radiolysis). Figures 3 and 4 show the shifts in equilibrium lines due to (3) salinity increase and (4) salinity and temperature increase. Furthermore, these diagrams do not address corrosion kinetics or mechanisms. Thus, in order to predict oxide growth one must consider the possible corrosion mechanisms and predict kinetics on the basis of theoretical extrapolation of short-term data.

## 2.2 Uniform Corrosion

Data. Rates for uniform corrosion in aqueous solution and soil calculated from experimental data are listed in table #1 along with some of the key experimental conditions. Most of these studies would indicate corrosion rates are low enough to protect waste in a 25-30 mm wall thickness overpack for many hundreds of years. However, Southwell and Alexander found the pitting rate to be about four times faster than the general corrosion rate (i.e. a "pitting factor" of 4). Romanoff found a pitting factor of 11 in soil. Accelerated localized corrosion mechanisms will be discussed in more detail later.

Rates for uniform corrosion of carbon steel in air and steam are listed in Table 2. Since these data were obtained at temperatures higher than repository conditions, the rates are probably higher unless the mechanisms are different. This study also suggests that in the corrosion by both air and steam, for the first 100 years of a canisters repository life less than 1 cm would have corroded.

Charlot and Westerman have also compiled a table of penetration depths of cast iron and carbon steel under acid, alkaline and neutral water and soil conditions (see Table 3). They find that if one allows a corrosion factor of five a canister would need to be 1.8 to 3.3 cm to last 1,000 years.

Radiation Effects. Physical effects will also cause alterations in predicted corrosion rates such that they may not be expected to meet regulatory criterion. Radiolysis is one such effect. Byalobzhesky states that radiation increases the rate of atmospheric corrosion of iron 10 - 100 times. He found the variation in rates to depend on three factors.

$$K = F(E_r, E_d, E_{p_h})$$

$E_d$  is the destructive effect of particulate radiation. It induces lattice defects in both metal and oxide.  $E_{p_h}$  is the photo-radiation effect. Although theoretically useful, its effect on general corrosion is negligible. Alpha, beta and neutron radiation from high level waste will be minimal; gamma-rays

will be the primary radiation. Thus,  $E_r$ , the effect of radiolysis, will be the most important influence of radiation in this study. The result of radiolysis is a shift in chemical potential of the corrodant due to radiolytic products.

Glass has reviewed radiolysis of water in connection with nuclear waste storage in repositories. He concludes that water irradiated by gamma-rays yields primarily the following distribution of products:

$$\begin{aligned}g(\text{H}\cdot) &= 0.60^* \\g(\text{H}_2) &= 0.45 \\g(\text{H}_2\text{O}_2) &= 0.75 \\g(\text{H}_3\text{O}^+) &= g(\text{e}^- \text{eq}) = g(\cdot\text{OH}) = 2.6 + 0.3 \\g(\text{H}_2\text{O}\cdot) &= 0.02 \\(\text{O}_2 \text{ absent})\end{aligned}$$

These figures are roughly independent of pH (Glass). However, if any dissolved oxygen is present, the concentration of hydrogen peroxide and other oxidizers will increase. (Two orders of magnitude for 1.5 ppm over concentrations at 0 ppm  $\text{O}_2$ ) (Townsend).

Radiolysis will also affect gases trapped in the backfill near a container. Glass (Ref. 16) predicts radiolysis products of air to include ionic oxygen ( $\text{O}_2^+$ ,  $\text{O}_2^-$ ,  $\text{O}_4^+$ ,  $\text{O}_4^-$ ), ionic clusters ( $\text{O}_2^- (\text{O}_2)_n$ ), and ozone ( $\text{O}_3$ ). Oxides of nitrogen will also be formed:  $\text{N}_2\text{O}_5$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ . This will result in nitric acid presence in wet oxide films. Water vapor will not be affected by radiolysis to any great extent due to the efficiency of back reactions for the intermediates.

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\* $g(x)$  = A primary yield established by inference.  $G(X)$  = the total yeild established by observation.  $G = 100/w \times m/n$  where  $w$  = energy used/ion pair,  $m$  = molecules altered,  $n$  = ion pairs formed.

In sum, gamma radiation will result in several changes in the iron system occurring simultaneously. The production of hydrogen will tend to reduce corrosion by creating a reducing atmosphere. The presence of strong cathodic depolarizers such as  $H_2O_2$  and  $O_3$  will greatly enhance corrosion. The hydrogen will most likely diffuse out of the system leaving an oxidizing environment.

Molecke (1981) shows that the overall effect of radiation is to accelerate general corrosion rates. Table 4 shows Molecke's data on the effect of gamma radiation on carbon steel in harsh brines. If salts in basalt water are concentrated by the heat from the waste products prior to full resaturation, containers may well be subjected to conditions similar to these brines.

Heat Transfer. Another important parameter effecting corrosion is heat flux at a corroding surface. Stepanov and Strokan in their studies of heat transfer walls holding seawater in desalination plants, show that increasing the heat flux at a metal increases its corrosion rate. This occurs for several reasons.

- (1) It accelerates diffusion processes and electrochemical reactions.
- (2) It changes the degree of protection provided by passivating layers.
- (3) It produces thermogalvanic cells (with hot spots acting as anodes).
- (4) It produces thermal stresses.
- (5) It promotes salt deposition on or near the heat transfer surfaces and hence concentrates brine altering Eh and pH.

Even at small heat fluxes, the corrosion of carbon steel has been shown to increase markedly. Pits are also shown to develop at temperature differentials of 15 - 20 degrees (Stephanov and Strokan).

Butler and Ison propose that under heat transfer conditions the type of attack may differ from that of general corrosion. Under acidic conditions,

they cite corrosion rate increases of 1100% for samples under a thermal gradient along the metal surface, compared to those in isothermal conditions.

Yasuda et al. also show that in caustic solutions, although carbon steel may be passive isothermally, it is corroded under heat transfer conditions. Localized corrosion is found to be the dominant corrosion mode in dilute solutions under temperature differentials of 1.7° to 12.4°C. (These differentials correspond to thermal fluxes of  $4 \times 10^4$  and  $4 \times 10^5$  kcal/m<sup>2</sup>-hr respectively. The test solution has 0.1 m NaOH which yields 4000 ppm anions. This is 9 times more concentrated than fresh basalt water and also contains dissolved O<sub>2</sub>). After 50 hours, pitting depth ranged an average 5 to 10 um with a maximum pit depth of  $40 \times 10^{-6}$  m.

Results from these articles do not allow one to quantify the expected increase heat transfer will cause in predicted corrosion rates in a repository. However, the testing for this effect is indicated. In addition, steam boiler technology, not reviewed here, provides a wealth of long-term data for carbon steel performance in anoxic alkaline water. This data should be reviewed, particularly the data concerning corrosion under sludge deposits, since this may be typical of the environment created by the backfill.

Oxide and Backfill Properties. Another factor which may modify corrosion rates is variation in iron oxide properties over time or under dynamic conditions. Key properties in determining oxide protectiveness are:

- (1) conductivity of bentonite or other backfill as well as the wetted porous corrosion scale on the iron,
- (2) adherence and integrity,
- (3) solubility of oxides and other corrosion products,
- (4) chemical/physical structure.

Because corrosion is fundamentally an electrochemical process, electrical conductivity of a saturated bentonite clay mixture is a key parameter in determining the corrosiveness of the basalt repository system. Evidence from ship wrecks buried in deep sea beds (Johnson, Barkman) and steel piling corrosion tests in Danish harbors (Arup and Glatz). indicate very slow general corrosion rates for cast iron in saturated soils although some cannons and ship hulls are pitted through. Logan (Logan) shows that in soils corrosion decreases rapidly with increasing resistivity (see Figure 5). Considering a saturated bentonite clay in the perspective of this chart, one can assume an upper bound conductivity of pristine Basalt water of 1,250 umho-cm (Anderson). This places Basalt in the 5 mg/dm<sup>2</sup>-day range; a low corrosion rate relative to soils of higher conductivity. However, this is just an estimate of bentonite conductivity. Data should be gathered to include effects such as radiolysis. A potential source for these data are studies involving the cathodic protection of cast iron piping in soils. For example, it is known that a current density of 0.1-5 mA/cm<sup>2</sup> is needed to electrically connect pipe with a sacrificial anode (Pourbaix).

In addition to the conductance of the backfill, the flux of ions through the oxide film on the waste canister will be proportional to the corrosion rate of the base metal. Thus a porous oxide will be less protective than a dense layer with fine pores (Feigenbaum). In addition, if an oxide conducts electronically, the potential gradient across the oxide will be kept at a minimum reducing the protective quality of the film. Table 5 compares density, conductivity and other characteristics of iron oxides (Anderson).

In sum knowledge of the range of porosity and resistivity of actual corrosion films on canisters would be desirable as an aid in predicting the protectiveness of the iron oxides and hence in determining a corrosion rate correlation.

As straight forward as this may appear, determining the morphology of the corrosion film that will be present on a canister in a repository in order to run tests on it is not a simple matter. First of all, canisters entering a repository will have an oxide already on them. This oxide will have been formed after canister fabrication, then will have been heated to 1000°C as the vitrified

waste was poured into it, and will be cooled slowly to ambient temperatures. The nature of the oxide film formed is unknown. However, one can guess that it may be similar to a millscale left on steel plates after hot rolling. Evans points out two possible scenarios in corrosion under mill-scales. If the mill-scale is loose, cracks in the film may initiate localized attack initially, but this attack will undermine the flakes of scale to produce a smooth protective general corrosion film. On the other hand, in cases where mill-scale is very adherent, aggressive pitting will occur at cracks and may lead to spalling.

To illustrate the degree to which surface condition may affect corrosion rate, Southwell et al. exposed unalloyed low carbon steel to a tropical marine environment for 8 years. They found that a pickled surface was about 10% more protective than mill-scale against uniform corrosion and about 15% more protective against pitting. Contrary to these results however, Butler & Ison found that pitting depth increased by a factor of 2 for a pickled surface over an untreated surface (Butler and Ison). A four month Belgian study of cast irons in a humid clay atmosphere showed a corrosion increase from 51 mg/dm<sup>2</sup> weight loss to 234 mg/dm<sup>2</sup> for grade 42 iron when mill-scale was removed. Similarly, grade 60 iron corrosion increased from 88 to 275 mg/dm<sup>2</sup> when mill-scale was removed (Dresselaers)\* All that can be concluded from this then, is that much depends on the nature of the scale (Evans). Canister processing may need to be tailored to produce a desirable scale. Corrosion tests should include the scales expected on production containers.

Assuming an optimal corrosion film, to determine long term behavior in a repository, specific information is needed about scale adherence properties, integrity (ability to withstand stresses without cracking or undulating) and the chemistry of local repository water attacking cracks in the film.

Within the literature, there are discrepancies as to whether or not a high temperature alkaline environment will produce an adherent scale. Huijbregts et al. have shown evidence that in either deaerated (4 ppb O<sub>2</sub>) or undeaerated

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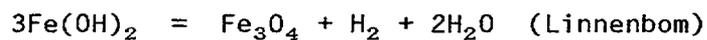
\*Note if comparing these data to rates in Table 1, Dresselaers added an artificial defect to his specimen.

weakly alkaline ( $3 \times 10^{-2}$  to  $10^{-5}$  N NaOH), 250-300°C solutions produced loose spalling oxide (Huijbregts). In a similar, 3 month test, Potter and Mann saw some spalling on samples, but not all. The double layered oxide formed in this experiment were described as partially protective. Testing conditions were 5-20 wt% NaOH, 250-355°C on mild steel; rate kinetics were parabolic (Potter and Mann). Effertz has found oxide to be double layered and protective without spalling when produced by high pressure water or superheated steam (250-600°C) at 30 ppb  $O_2$ . Steam and water formed oxides of different morphology, but both formed in accordance with parabolic rate laws (Effertz). Alloying elements also effect the adherence of an oxide film. Chromates in stainless steel and silicates in wrought iron form very tight protective films (Latanision; Butler and Ison). In plain carbon steels and irons, however, Tylecote indicates that the higher the degree of purity, the more adherent and strong the corrosion film. He attributes this to a decrease in preferentially oxidizable impurities accumulating and causing stress at the metal/oxide interface (Tylecote). The level of purity to which Tylecote refers is spectral grade, and thus this may have little application to the large scale manufacture of waste containers.

Many studies indicate very little difference in the corrosion behavior of low alloy steels versus the irons (Huijbregts, Reinhart). However, in soil media, grey iron has been found to be more protective than malleable irons by a factor of ten (Bureau of Reclamation, 11965). Grey iron is also superior to ductile iron or carbon steel in uniform corrosion, although it is much less resistant to localized attack (Hudson and Watkins). This may however, be more a function of the integrity of the graphite matrix left after graphitization processes have leached out the iron, than a function of low corrosion kinetics (Latanision). Thus in the presence of radiolysis and heat transfer, which make electrolytes more aggressive, it is better to use a material such as a carbon steel which is not vulnerable to graphitization (dissolution of the metal in cast iron to produce a "skeleton of graphite flakes).

Determining the solubility of oxides and chlorides in basalt water will be important in determining loss of iron that does not add to further protection via corrosion film (Berge; Gadiyar). Gadiyar and Elayathu have studied corrosion

in terms of percentage of adherent oxide. Their figures show about 70% adherence (i.e. about 30% loss to environment, see Table 1 for experimental conditions) (Gadiyar and Elayathu). Similarly, Huijbjegts et al. show about 50% nonadherent oxide. A probable mechanism to explain this loss involves the oxidation of iron to ferrous hydroxide (Fe(OH)<sub>2</sub>). Ferrous hydroxide is usually produced as Fe<sup>+2</sup> and OH<sup>-</sup> ions. Thus it is highly water soluble (see Table 6). At ambient temperatures and anoxic conditions, it is the primary corrosion product (Bloom, Linnenbom). At high temperatures (60-250°C), ferrous hydroxide will rapidly oxidize to magnetite via the Schickor reaction:



This may occur near the substrate and magnetite will precipitate on the existing oxide film as a loose, flakey oxide (Huijbiegts) or it may occur at some distance from the metal (Gadiyar and Elayathu).

The Schickor reaction is also reversible and in a hydrogen enriched atmosphere, magnetite is susceptible to partial reduction to ferrous hydroxide (Berge). Under experimental conditions simulating a PWR loop (high temperature, alkaline, low O<sub>2</sub> level), the soluble iron content was found by Berge et al. to be proportional to the concentration of dissolved hydrogen to the power 1/3. Other experiments have derived lower values for percentage soluble iron produced by H<sub>2</sub> (Berge). An additional possibility in this situation is complete reduction of magnetite back to iron (Barkman). This would not be expected in a repository.

### 2.3 Localized Corrosion

Localized attack, more specifically pitting or crevice corrosion, is mechanistically similar to uniform attack. An oxygen concentration cell is established with a small oxygen starved anode and a large oxygen rich cathode. The anode is kept from contact with the bulk electrolyte by a long narrow transport path in a crevice, or a thin mushroom film of corrosion products over a pit. The absence of oxydizer within these occluded cells allows the hydrogen ion concentration to rise and attracts aggressive ions such as chloride into

the pit to maintain electroneutrality. Acid, usually hydrochloric acid, builds up in the anode accelerating metal dissolution (Pourbaix, Gadiyar, Piccinini).

Figure 6 shows the effect chloride ions at 355 ppm has upon the Pourbaix diagram. In comparison, Table 6 shows anion and cation concentration levels in basalt water. In addition to chloride ions, the only other potentially aggressive species is fluoride (Newby et al, 1982). However, Ogura and Ohama have found that fluoride ion does not induce pitting in iron even at concentrations of 950 ppm (Ogura and Ohama).

Propagation. Many factors render metals susceptible to localized attack. These include defects and microinhomogeneities within the oxide, stresses within the base metal, and surface abrasions (Evans, Townsend, Kruger).

Mechanistically, there are many explanations to account for protective film breakdown and the establishment of an autocatalytic occluded cell. Kruger and Hardman have compiled and assessed these theories, and provide two which are particularly applicable to ion pitting propagation (Kruger).

The first, by Galvele is very detailed. Pits are assumed to initiate at transient breaks in the film produced by mechanical or electrochemical means. Before the oxide has an opportunity to heal the passive layer, hydrolysis occurs, lowering the local pH. If acidification at this point is sufficient to prevent repassivation, the pit will grow. If conditions can be specified well enough using a Pourbaix diagram one can estimate regions at which metal dissolution can occur and the pits that will exclude repassivation. This allows one to gather insights into the pitting rate as a function of potential. This model explains the existence of empirically established Pourbaix protection potentials as well as corrosion or open circuit potentials characteristic of metals (Pourbaix, Galvele).

The second model, by Rosenfeld and Danilov, is an absorbed ion displacement model. In it, chlorine displaces oxygen in the intersities of the oxide and, in very localized sites, chlorine will migrate to the base metal creating an anode. Metallic dissolution produces the mushroom of corrosion products

(mostly  $\text{Fe}(\text{OH})_2$ ) needed to isolate the cell. From there, crevice corrosion mechanisms become operative (Rosenfeld and Danilov).

A crevice corrosion model particularly applicable to iron is the four stage model proposed by Oldfield and Sutton (Oldfield and Sutton).

Stage 1: Uniform corrosion reactions take place both within and without the crevice. Eventually, corrosion products build up in the crevice providing only a tortuous diffusion path for oxygen. Inside the crevice, oxygen supply is depleted and a concentration cell is established. (Note in the pitting model this is analogous to the production of corrosion products around a pit.)

Stage 2: Metallic dissolution continues within the crevice; ferrous ions scavenge hydroxides; hydrogen ion concentration rises. Reduction of oxygen continues outside the crevice. Chloride ions migrate into the crevice to maintain electroneutrality. Ferric (formed from passive iron) and ferrous (formed from active iron) ions combine with chlorine ions.

Stage 3: The concentration of  $\text{Cl}^-$  and  $\text{H}^+$  within the crevice reaches a level that prevents any repassivation of oxide on crevice walls. Accelerated corrosion begins.

Stage 4: Crevice corrodes rapidly. Hydrogen may evolve leading to hydrogen embrittlement and stress corrosion cracking even in iron (Toensend, Oldfield).

If crevice geometry, critical HCl levels to inhibit repassivation and passivating current can be specified, this crevice corrosion model can predict one of two outcomes: (1) pH level will be controlled by mass transport of  $\text{FeCl}_2$  from the crack, (2) pH will drop further and corrosion rate will accelerate (Rosenfeld and Danilov).

Given the presence of chloride ions, the necessity of welds or mechanical closure for canisters, and the geologic periods of time for which container integrity must be maintained, occluded cell corrosion is of very serious concern. The three elegant models above are difficult to apply quantitatively, since

repository conditions can not be accurately specified at this time. However, one can predict that propagation will occur. Defects within an oxide layer cannot be completely avoided even under the best of conditions. Chemical microinhomogeneities can be reduced drastically by vacuum arc remelting or electroslag remelting of the carbon steel/cast iron to remove impurities. Yet localized stresses and scratches can not be avoided. Stresses, particularly in the heat affected zone about a weld are perhaps the most severe weakness in a canister. Cramer and Carter provide data for carbon steel weld corrosion in deaerated, hot, harsh brine (primarily NaCl). See Table 7. The weld itself corroded at rates similar to the control specimen. However, in the heat affected zone, corrosion rates as high as 920 um/year (for E7016) are reported (Cramer and Carter).

The welds analyzed in Table 8 are in a solution far more saline and acid than is expected for a basalt repository. However, these specimen are small (2.5 x 2.5 cm) and show a -5% to +43% change in corrosion damage (Cramer and Carter). This indicates that similar changes might be expected for the thick welds (up to 25 cm) considered in the past for BWIP.

Cramer and Carter also ran field test on these welded specimen for 45 days. Carbon steel suffered very deep pitting, particularly in the heat affected zone. The 4130 steel was penetrated in the heat affected zone in both brine and steam (Cramer and Carter). Because the general corrosion rates in geothermal brine are so high, pitting factors were low relative to Romanoff's data (note ratio of pitting to general corrosion rates for data in Table 1), which range from 2.2-4.8. However, these geothermal brines can not readily be used to model behavior in basalt, particularly since it is not known to what extent dissolved gases (CO<sub>2</sub>, SO<sub>2</sub>, etc.) were responsible for corrosion rates.

Mechanical closure will also provide a crevice for occluded cell attack. If the closure will be sealed with a weld, one can calculate from the weld thickness the time needed for general corrosion (or more quickly, localized) processes to expose it to the bulk electrolyte.

Scratches provide sites for attack because of the stresses induced in the metal when they are formed. Tensile stresses will render part of the metal anodic relative to the unstressed areas. These stresses can crack the oxide layer, leaving the metal exposed to attack (Evans). Evans notes that scratches repassivate in iron more readily than in steel (Evans). However, with Mears he found that if a scratch has a load on it, probability of corrosion occurring increases. (19 to 52% with a mass increase from 100 to 800 gm (Mears and Evans). Loaded scratches will be present in a repository. For example, a current BWIP design places canisters on two metal railings (see Appendix). Minor loads produced by crushed basalt pressed against the container by a water-swollen backfill may not affect general corrosion rates severely although they could be sites for localized corrosion.

Growth of pits and crevices. Ultimately, one should assume that pits will propagate on waste containers. Then one is left with the question of how fast and how deep these pits will grow. Factors that control pitting have been empirically determined from extensive data taken at the National Bureau of Standards. For ferrous metals these are summarized in a equation for maximum pit depth (P) in mils (Newby 1982):

$$P = K_n K_a (10 - \text{pH})^n (t/p)^n A^a$$

where:  $K_n$  = soil aeration factor. 170, 222 or 355 for soils that are well, fairly well, and poorly aerated respectively.

$K_a$  = 1.06 for steel and 1.40 for cast iron

$n$  = soil aeration power 1/6 for well aerated soils  
 1/3 for fairly well aerated soils  
 1/2 for poorly aerated soils  
 2/3 for poorly aerated soils with soluble corrosion products

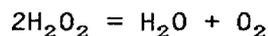
$t$  = time in years

$p$  = soil resistivity in ohm-cm

A = exposed surface area in ft<sup>2</sup>

a = 0.16 for steel and 0.22 for cast iron

In a repository situation radiolysis can, at least in principle, reduce localized corrosion rates. Radiolysis in a crevice can consume H<sup>+</sup> at the same time it increases the pH in the crevice and the H<sub>2</sub>O<sub>2</sub> reduces the differential by the reaction:



Both consumption of H<sup>+</sup> and production of O<sub>2</sub> in the occluded region tend to slow down further corrosion. In addition, these conditions establish a protective oxide film on the inside of the occluded cell (Pourbaix, Townsend). In other words, the repassivation effects of the O<sub>2</sub> will compete with the Cl<sup>-</sup> breakdown effects. Townsend puts these protective mechanisms into perspective by showing that additions of NaCl at 1 ppm overcome the passivating effect of 3000 ppm H<sub>2</sub>O<sub>2</sub> (Townsend).

Radiolysis will also supply H<sub>2</sub> and H<sup>+</sup> within a pit (Glass). Hydrogen radical will readily combine, perhaps with the H<sup>+</sup> available in solution to produce hydrogen. Also, if the hydrogen potential inside the pit is low enough to generate hydrogen gas from the solution, then anodic reactions will produce H<sub>2</sub> (Pourbaix). The effect of H<sub>2</sub> from either or both of these sources will be to restrict the decrease in pH (by scavenging excess H<sup>+</sup>). However, it may lead to hydrogen embrittlement and to increased solubility of magnetite (Townsend, Berge).

What the net effect of radiation on localized corrosion will be in the long term is as yet unknown.

The conclusions to be drawn from a literature assesment of localized corrosion per Carter's recommendation, is that analysis upon which licencing decisions are to be based need to be highly specific and incorporate as many aspects of the system as possible (i.e., welds, radiation, electrolyte and steam flow, dissolved gases, pressure). If it is possible, field testing should be accomp-

lished to verify what failure modes and corrosion rates will be (Carter J. P. 1982).

#### 2.4 Stress Corrosion Cracking and Hydrogen Embrittlement

Cast iron and carbon steel can suffer failure by stress corrosion cracking (SCC) under highly caustic environments and mechanical tensile stresses. Current theory uses a variety of mechanisms to describe all the characteristics and modes of SCC. These can be segregated into roughly three categories: cracks which are associated with either (a) pre-existing active paths; (b) strain generated active paths; or (c) specific absorption at subcritical stress sites (Parking).

Pre-existing active paths in an alloy are formed by microsegregation and precipitation within a metal, usually at grain boundaries. Local galvanic cells are established weakening the metal against mechanical failure. Microsegregation can be minimized by proper melting practice and careful consideration of casting technique. Precipitation can be minimized by keeping alloy content low and removing sulfur (Parking).

Strain generated active paths usually initiate at slip steps occurring at the surface of the metal. SCC proceeds intergranularly. Specific absorption paths require absorption of gases (particularly  $H_2$ ) into tiny cracks on the surface of the metal (Parking).

The role of hydrogen in SCC is not explicitly defined, although it is clear the  $H_2$  embrittlement will render a metal susceptible to SCC (Logan and Yolken). In some cases if metal is in a strained condition, hydrogen will reduce the metal's yield strength to the point where it can fail mechanically (Bhat).

The rate of hydrogen diffusion into a metal and the depth of attack (decarburation and fissuring) varies with metal heat treatment,  $H_2$  pressure, atmospheric moisture content and temperature (Logan, Bhat, Gutzeit). There exists an incubation period for attack, although it is shortened considerably by water vapor. Water vapor also increases the depth of hydrogen attack. However,

Gutzeit and Thygeson report attack depths which logarithmically approach only a few millimeters (Gutzeit).

Solution chemistry and mechanical strength also plays a dominate role in the modes of SCC. In aqueous chloride environments, for example, SCC is dependent on the yield strength of the alloy. Probability of failure increases for steels with strengths greater than 689 MN/m<sup>2</sup> (100,000 psi), while steels less strong appear uniformly resistant. Cracking rate increase with temperature and Cl<sup>-</sup> concentration, but the critical stress factor (K<sub>ISCC</sub>) does not.

In sodium hydroxide solutions cracking is known to occur at concentrations above 5 wt% and at temperatures between 100°C and 350°C. Presence of oxygen increases metal susceptibility and crack growth rate. Carbonates present in basalt water may help inhibit SCC in NaOH (Newby 1982). The low alloy cast irons and steels being considered for waste canisters will have strengths less than 689 MW/m<sup>2</sup> (Newby 1982). It will need to be determined though whether hydroxide concentration could increase from 1.4 ppm (in pristine basalt water) to 1100 ppm (5 wt%) within the time that the canister is above 100°C and oxygen is present.

Recent tests on stainless steels indicate the radiation effects on SCC can not be ignored. Fugita et al. find that radiation can have both beneficial and deleterious effects. Furthermore, the interaction between oxygen and radiolysis products has a very complex effect on SCC.

## 2.5 Galvanic Corrosion

Galvanic interactions are caused by metals in electrical contact having different corrosion potentials and thus establishing an electrochemical cell. There should be little reason to worry about this though, if waste canister, overpack, and metal rail upon which the canister is to be seated are all of the same material. Weld metal should also be chosen with care to avoid galvanic potential. However, if a titanium overpack is used and it comes into electrical contact with iron, iron will be anodic. Ferrous ions will be produced and react with water to form hydroxides. This will release hydrogen which will embrittle the titanium.

## 2.6 Bacterial Corrosion

Microbial induced corrosion is a major concern for subterranean metals. In Belgian mines for example, over a 90 year period iron supports suffered corrosion 50% of which was believed to be attributable to bacterial action (Dresselaers).

The so called "iron" bacteria are a miscellaneous group which are associated with the oxidation of ferrous ions to ferric ions. They tunnel through metal creating "tubercles" within pipes. They also accumulate as waste, masses of ferric hydroxide and biological deposits which mechanically strengthen the tubercles. As the tubercles thicken and more wastes are built up, influx of water and oxygen are restricted thus setting up a differential aeration cell (Olsen, Iverson).

Most of the iron bacteria are autotropic and anerobic. Common genera include *Ferrobacillus*, *Gallionella* and *Sphaerotilus* (Iverson). *Desulfovibrio desulfuricans* and related species also reduce iron but require sulfate in the soil around the iron. They oxidize iron into  $Fe^{+3}$  and produce sulfuric acid from sulfate. Most of the "sulfate" bacteria are autotropic and anerobic, although some require small amounts of organic matter and water (Hunter).

Anaerobic bacteria are known to live in pH ranges 5.0 - 9.0 (Hunter). Thus, some could be expected to thrive in the water surrounding the waste canister. Furthermore, while the canister remains above the boiling point of water, very few bacteria could be expected to remain near it. Radiation given off by the waste will also kill bacteria (Gause).

## 2.7 Conclusions

In summary, there are several conditions present in a repository that will have major effects on corrosion rates, most of these deliterious. These are heat transfer gradients, radiation, and oxygen supply from air shafts.

- (1) Heat transfer will not only accelerate corrosion due to its effect on the metal canister itself, but it will also concentrate the salts present in

repository waters to an unknown extent. A best case would be to assume that this concentration will be negligible; worst case is to assume that the waters reach saturation.

- (2) Radiation is known to accelerate general corrosion. Its effects on localized corrosion have been conjectured, but not proven.
- (3) Oxygen supply, even in very small amounts will have large effects on corrosion rates. In trying to estimate these effects, one can expect that oxygen will constitute 20% of the air prior to backfilling. Supply will diminish over time, although there is question as to when premining conditions will be reestablished.

The dominant mode of corrosive attack expected is occluded cell corrosion. Of principal concerns are pitting in the heat affected zone around a welded closure as well as crevice corrosion in a mechanical closure and in loaded scratches such as those created by containers on metal railings or under loads induced by the packing materials. Accelerated pitting factors\* may be expected to range from 1 - 4 in a best case scenario (Braitwaite 1980, derived from O<sub>2</sub> free basalt water data) to 11 (Romanoff, 1968 derived from soil corrosion data).

General corrosion, whether it follows a linear or parabolic rate law, should not be a concern as a failure mode. The only concern would be the statistical distribution of container failures. Even if the average predicted corrosion rate for canisters is satisfactory to meet regulatory containment criterion, an unacceptable number might be expected to fail within the lifetime objective.

Stress corrosion cracking, galvanic corrosion and biodegradation will probably not be of concern as failure modes for waste canisters made from carbon steel.

### 3 REPOSITORY DESIGN

Provided here is a short summary of current BWIP research and development that is specific to the environment of waste containers. While these proposed

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\*A pitting factor is the ratio of the pitting to general corrosion rate.

designs do not necessarily reflect those that will be included in the license application, they do provide the reader with an idea of design parameters as well as a visual picture of a hard-rock repository and waste canisters.

Basalt is unusual in that the maximum horizontal stress in the rock is about twice as large as the vertical stress. Thus, horizontal emplacement of canisters into holes running between two large tunnels (drifts) is now favored over vertical emplacement with boreholes in the drift floor. Figure 7 illustrate storage panels between drifts (BWIP Project Veiv Graph 1982). Figures 8 and 9 give an example of a repository layout with dimensions.

Because of the requirements of 10 CRF 60 and in view of the complexity and uncertainty in predicting the long term reliability of geologic formations on inhibiting radionuclide migration from the repository, engineered barrier systems are being incorporated into repository design. These barriers are designed to protect the canister from corrosion and mechanical rupture, to inhibit leaching of waste from the canister and to sorb or fix any radionuclide which has leached out of the canister. Waste is to be incorporated in a stable ceramic/glass matrix within a canister. The canister is placed within a buffer-lined overpack container. The container is emplaced and backfilled (see Figure 10) (Refs. 62,63).

The idea of engineered barriers is supported by several BWIP findings to date:

- (1) Reversible backfill dehydration is a function of pressure.
- (2) Reducing environment retards nuclide migration.
- (3) Most radionuclides appear solubility limited.
- (4) Reducing conditions rapidly reestablish via hydrothermal basalt reactions (BWIP PProject View Graph 1982).

Figures 11 - 13 depict procedures for backfilling and sealing a repository. In particular, backfilling the main shaft into the repository (2000 feet underground) will be important to prevent oxygen from diffusing into the repository.

Backfilling of the individual boreholes may be done immediately once the canisters are emplaced, or a period of ventilation to dissipate heat produced by cesium and strontium may be provided for up to 50 years prior to backfilling (Ref. 63).

#### 4 CONTAINER DESIGN

The design concepts used by BWIP to develop a waste container are: waste package functions, emplacement conditions and design description (i.e., horizontal emplacement and simplified waste package). Tables 10 and 11 provide a view on BWIP functional design criterion called "work elements: Tables 12 - 14 describe canister functions and predicted environment (BWIP View Graph 1982).

The simplified waste package referred to is the three component system utilizing 77-26 borosilicate glass as the waste form, low carbon steel as the canister material, and 25% bentonite clay/75% crushed basalt backfill. It should be noted however, that other materials are being considered. Specifically, for canister fabrication these are: Titanium and Ticode 12, Inconel, Hastelloy, Cupronickel, Zircaloy and Stainless Steel (Smith; BWIP View Graph 1982). The reasons for concentrating on cast iron and carbon steel in this study, inspite of their known high corrosion rates are as follows:

- (1) They are inexpensive and can therefore be used in large sections (Charlot, Newby 1982, Gause, Newby 1981).
- (2) They are easy to fabricate and most steel are easy to weld (Charlot, Newby 1982, Gause, Newby 1981).
- (3) Our knowledge on the characteristics and long term reliability of carbon steels and iron has been built up over centuries (Johnson).

Figures 14 and 15 provide an example of one canister construction and emplacement design. In general, the canisters are prescribed to be very long relative to their diameter. Proposed wall thicknesses range from 4cm to 25cm (BWIP View Graph 1982, Newby 1982, Newby 1981).

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Table 1 Comparison of General and Pitting Corrosion Rates

Table 2 Corrosion of carbon steel in steam & air (Ref. 14)

Corrosive Medium	Temp. °C	Alloy	Penetration Depth after 10,000 hrs. (14 months) mm x 10 <sup>3</sup>	Rate in mm/yr
Air	454	A216	10.2	.009
		1029	14.5	.013
		1035	14.7	.013
		1116	33.0	.029
Air	538	A216	40.6	.035
		1029	50.8	.045
		1035	38.1	.033
		1116	71.1	.062
Steam	454	A216	8.64	.007
		1029	10.9	.009
Steam	538	A216	66.0	.058
		1029	30.5	.027
		1035	96.5	.085
		1116	55.9	.049

Alloy Identification

	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	V
A216	.30	1.00	.04	.045	.60	.50	.50	.40	.75	.403
1029	.25/.31	.60/.90	.04	.050	.35	--	--	--	--	--
1035	.32/.38	.60/.90	.04	.50	--	--	--	--	--	--
1116	.14/.20	1.10/1.40	.04	.16/.23	--	--	--	--	--	--

Table 3 Corrosion of carbon steel in steam and air (Ref. 14)

Materials: Cast Iron & Carbon Steel

Environment: Anoxic Brine

Overpack Lifetime (Years)*					
50°C	100°C	150°C	200°C	250°C	300°C
$2 \times 10^8$	$2 \times 10^7$	$4 \times 10^6$	$9 \times 10^5$	$3 \times 10^5$	$1 \times 10^5$

\*Lifetime defined as time to pit through a 30 cm overpack thickness and simultaneously consume 7.5 cm by general corrosion. Equations used are:

(1) General corrosion assumes parabolic kinetics:

$$x \text{ (mm)} = 32.6 \exp(-2850/T(^{\circ}\text{K})) t(y)^{.5}$$

(2) Pitting corrosion uses a pitting factor of four

$$x \text{ (mm)} = 130 \exp(-2850/T(^{\circ}\text{K})) t(y)^{.5}$$

Table 4 Estimated uniform metal penetration in  
cast iron and carbon steel (Ref. 2)

<u>Environment</u>	<u>Temp. °C</u>	<u>Rate Law</u>	<u>1000 yr Penetration Depth (cm)</u>	
			<u>Uniform</u>	<u>With Factor 5 Allowance</u>
pH 7 to 8, H <sub>2</sub> O	250	Parabolic	.38	1.90
13% NaOH	250	Linear	.38	1.90
Neutral H <sub>2</sub> O	250	Linear	.66	3.30
Soil	Ambient	Linear	.57	2.55

Table 5 The effects of radiation on uniform corrosion of 1018 steel (Ref. 18)

T = 90°C

Irradiation Rate (Rem/hr)	Solution	Test Duration (days)	Corrosion Rate (mm/yr)	*Corrosion rate w/o Radiation (mm/yr)
10 <sup>7</sup>	Brine B	79	1.00	.040
10 <sup>7</sup>	Brine A	79	1.00	.261
10 <sup>5</sup>	Brine A	49	0.10	.261
10 <sup>5</sup>	Seawater	49	0.03	---

\*Estimated from data given by Braithwaite and Molecke (Ref. 8), assuming linear kinetics between data points at 70°C and 250°C.

Table 6 Comparison of Oxide Attributes (After 29,30)

Table 8 Corrosion of weld and nonweld specimen  
in salton sea brine in mm/yr (Ref. 46)

---

Temperature: 232°C ppm Cl<sup>-</sup>: 155,000 pH: 6.1 at 25°C

Alloy/Filler Alloy	Nonweld	Weld deaerated	Heat Treated Weld
1020 C Steel/E6010	.419	.510	.520
1020 C Steel/E6011	.419	.380	----
1020 C Steel/E6012	.419	.420	.430
1020 C Steel/E6013	.419	.510	.540
1020 C Steel/E7016	.419	.520	.410
1020 C Steel/E7018	.419	.430	.460
1020 C Steel/E7024	.419	.600	.420
4130 Steel/E6010	.330	.430	.470
	oxygen at 100 ppm		
1020 C Steel/E6010	26.900	30.000	----
4130 Steel/E6010	25.400	28.400	----

---

Table 9 Summary of scenarios

Scenario	Maximum Penetration Depth after 1000 years (cm)			
	Carbon Steel		Cast Iron	
	general	pitting	general	pitting
I	---	---	2.3	9.2
II	---	---	3.6 - 11	8
III	1.9	10.4	0.6	15.2
IV	19 - 28	failure	---	---
V	failure	failure	---	---

Table 10 Typical waste package design work elements

Table 11 Data needed to satisfy design related work elements

Table 12 Waste-package component functions versus repository history for reference waste-package conceptual design

Table 13 Summary of repository conditions in basalt

Table 14 Expected repository conditions at the emplacement location

Figure 1 Pourbaix diagram for (Ref. 6)

Figure 2 Passivation (Ref. 6)

Figure 3 Potential pH diagram for iron  
in high salinity brine at 25 C.

Figure 4 Potential pH diagram  
for iron in high  
salinity brine at 250 C.

Figure 5 Corrosion of gray iron in soils of differing resistivity

Figure 6 Pourbaix diagram for iron with 355 ppm  $\text{Cl}^-$

At pH 8 this can be interpreted as: (Ref. 6)

- 1 = general corrosion of nonpolarized iron in anoxic solution.
- 2 = pitting of nonpolarized iron in oxidic solution.
- 3 = active pits or crevices.

Figure 7 Dimensions of a repository drift

Figure 8 Typical crosssection of repository

Figure 9 Dimensions of boreholes between drifts

Figure 10 Borehole design

Figure 11 Backfilling Main Shaft of Repository

Figure 12 Backfilling of borehole

Figure 13 Backfilling a large drift

Figure 14 Canister construction with dimensions

Figure 15 Canister emplacement







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Table #1 Comparison of General and Pitting Corrosion Rates

Material	Soil or Solution:	Synthetic Basalt	Fresh Water	LiOH	LiOH	1% NaCl	Brine "A"*	Sagamor WA Loam	Hanford Loam
	Oxygen:	50ppb-1 ppm	OXIC	<0.05 ppm	3.5 ppm	<0.01 ppm	~30 ppbO <sub>2</sub>	Aerobic	Aerobic
	ppm Cl-:	50	70	0	0	6,000	300,000	/	/
	TDS* or pH	6.7 pH 425ppmTDS (10.5 pH at 25°C)	1000 ppm TDS	10.5 pH	10.5 pH	4.8 pH	525,555 ppm TDS	8.8 pH	~8.8 pH
	Temperature:	250°C	25°C	310°C	310°C	250°C	250°C	Ambient	Ambient
	Test length:	/	16 Years	22 days	9.2 months	~11 days	28 days	8 Years	17.5 years
	Reference:	Braithwaite & Molecke 1980 (8)	Southwell & Alexander 1970 (9)	Gadiyar & Elaythu 1980 (10)		Shannon (11) 1977	Braithwaite Molecke 1980 (8)	Romanoff 1958 (12)	Romanoff 1957 (13)
Carbon Steel (rate in mm/yr)	Overall	/	0.04	.0167	.0039	a) 0.3 b) 0.2	1.70	.02	/
	Pitting	/	0.16	/	/	/	/	.22	/
Cast Iron (rate in mm/yr)	Overall	a.0241 d.0171 b.1145 e.0265 c.0201	0.05	/	/	/	/	.0068	.0091 .0075
	Pitting	/	0.17	/	/	/	/	.32	/
Miscellaneous	*TDS = Total Dissolved Solids	average of two data points alloy I.D. a. B-7 (ductile iron) + .73 Cu b. 22-8 ductile iron + .68 Cr 1.34 Cu c. 142-12 grey iron + 1.1663 - grey iron e. 136-4 grey iron + 3.05 Ni	Cast Steel 0.27 C  3.2 C Grey Iron	Analysis of Steel .119 C, .35Mn, .03P, .03S, .04Si  Average of 7-10 specimen		Alloy 10 a) .13C, .42Mn, .008P, .017S  b) .44C, 1.56Mn, .008P, 0.17S, .21Si, .21Mo	1018 Steel  *Brine "A" is about 9 times more saline than seawater (in molarity)	Soil Not Solution	

Table #6 Comparison of Oxide Attributes (After 29,30)

<u>Composition</u>	<u>Mineral Name</u>	<u>Electrical Resistivity</u>	<u>Density gm/cm<sup>2</sup></u>	<u>Thermal Behavior</u>	<u>Chemical Stability</u>
$\text{Fe(III)}_2$	----	Insulator	3.40	Decomposes at 100°C to magnetite	<ul style="list-style-type: none"> <li>• Stable only in absence of O<sub>2</sub>.</li> <li>• Highly soluble in water.</li> </ul>
$\text{Fe}_3\text{O}_4$	Magnetite	Electrical Conductor	5.20	Stable to 1597°C	<ul style="list-style-type: none"> <li>• Insoluble in high temperature water.</li> <li>• May be partially reduced by hydrogen to ferrous hydroxide.</li> </ul>
$\gamma\text{-Fe}_2\text{O}_3$	Maghemite	Semiconductor to insulator	4.88	Transforms to hematite above 250°C	<ul style="list-style-type: none"> <li>• Water causes conversion to hematite at lower temperature.</li> </ul>
$\alpha\text{-Fe}_2\text{O}_3$	Hematite	Insulator	5.25	Decomposes to magnetite at 1459°C and 1 atm	
$\gamma\text{-FeOOH}$	Lepidocrocite	Insulator	3.97	Dehydrates to maghemite above 200°C	<ul style="list-style-type: none"> <li>• Water causes conversion to maghemite at lower temperatures.</li> </ul>
$\alpha\text{-FeOOH}$	Goethite	Insulator	4.20	Dehydrates to hematite above 200°C	<ul style="list-style-type: none"> <li>• Water causes conversion to hematite at lower temperatures.</li> </ul>

Table 1 Comparison of General and Pitting Corrosion Rates

Table 2 Corrosion of carbon steel in steam & air (Ref. 14)

Corrosive Medium	Temp. °C	Alloy	Penetration Depth after 10,000 hrs. (14 months) mm x 10 <sup>3</sup>	Rate in mm/yr
Air	454	A216	10.2	.009
		1029	14.5	.013
		1035	14.7	.013
		1116	33.0	.029
Air	538	A216	40.6	.035
		1029	50.8	.045
		1035	38.1	.033
		1116	71.1	.062
Steam	454	A216	8.64	.007
		1029	10.9	.009
Steam	538	A216	66.0	.058
		1029	30.5	.027
		1035	96.5	.085
		1116	55.9	.049

Alloy Identification

	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	V
A216	.30	1.00	.04	.045	.60	.50	.50	.40	.75	.403
1029	.25/.31	.60/.90	.04	.050	.35	--	--	--	--	--
1035	.32/.38	.60/.90	.04	.50	--	--	--	--	--	--
1116	.14/.20	1.10/1.40	.04	.16/.23	--	--	--	--	--	--

Table 3 Corrosion of carbon steel in steam and air (Ref. 14)

Materials: Cast Iron & Carbon Steel

Environment: Anoxic Brine

Overpack Lifetime (Years)*					
50°C	100°C	150°C	200°C	250°C	300°C
$2 \times 10^8$	$2 \times 10^7$	$4 \times 10^6$	$9 \times 10^5$	$3 \times 10^5$	$1 \times 10^5$

\*Lifetime defined as time to pit through a 30 cm overpack thickness and simultaneously consume 7.5 cm by general corrosion. Equations used are:

(1) General corrosion assumes parabolic kinetics:

$$x \text{ (mm)} = 32.6 \exp(-2850/T(^{\circ}\text{K})) t(y)^{.5}$$

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$$x \text{ (mm)} = 130 \exp(-2850/T(^{\circ}\text{K})) t(y)^{.5}$$

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cast iron and carbon steel (Ref. 2)

<u>Environment</u>	<u>Temp. °C</u>	<u>Rate Law</u>	<u>1000 yr Penetration Depth (cm)</u>	
			<u>Uniform</u>	<u>With Factor 5 Allowance</u>
pH 7 to 8, H <sub>2</sub> O	250	Parabolic	.38	1.90
13% NaOH	250	Linear	.38	1.90
Neutral H <sub>2</sub> O	250	Linear	.66	3.30
Soil	Ambient	Linear	.57	2.55

Table 5 The effects of radiation on uniform corrosion of 1018 steel (Ref. 18)

T = 90°C

Irradiation Rate (Rem/hr)	Solution	Test Duration (days)	Corrosion Rate (mm/yr)	*Corrosion rate w/o Radiation (mm/yr)
10 <sup>7</sup>	Brine B	79	1.00	.040
10 <sup>7</sup>	Brine A	79	1.00	.261
10 <sup>5</sup>	Brine A	49	0.10	.261
10 <sup>5</sup>	Seawater	49	0.03	---

\*Estimated from data given by Braithwaite and Molecke (Ref. 8), assuming linear kinetics between data points at 70°C and 250°C.

Table 6 Comparison of Oxide Attributes (After 29,30)

Table 7 Basalt groundwater (Ref. 4)

Ion	Concentration (ppm)	Millequivalents
Na <sup>+</sup>	250	10.870
K <sup>+</sup>	1.9	.050
Mg <sup>2+</sup>	0.04	.004
Ca <sup>2+</sup>	1.3	.066
CO <sub>3</sub> <sup>-2</sup>	27	.900
HCO <sub>3</sub> <sup>-</sup>	70	1.148
OH <sup>-3</sup>	1.4	.082
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	103	1.084
Cl <sup>-</sup>	148	1.096
SO <sub>4</sub> <sup>-2</sup>	108	2.250
F <sup>-</sup>	37	2.176

$H_3SiO_4^-$  ←  
 $SO_4^{-2}$  ←  
 $F^-$  ←

Table 8 Corrosion of weld and nonweld specimen  
in salton sea brine in mm/yr (Ref. 46)

---

Temperature: 232°C ppm Cl<sup>-</sup>: 155,000 pH: 6.1 at 25°C

Alloy/Filler Alloy	Nonweld	Weld deaerated	Heat Treated Weld
1020 C Steel/E6010	.419	.510	.520
1020 C Steel/E6011	.419	.380	----
1020 C Steel/E6012	.419	.420	.430
1020 C Steel/E6013	.419	.510	.540
1020 C Steel/E7016	.419	.520	.410
1020 C Steel/E7018	.419	.430	.460
1020 C Steel/E7024	.419	.600	.420
4130 Steel/E6010	.330	.430	.470
	oxygen at 100 ppm		
1020 C Steel/E6010	26.900	30.000	----
4130 Steel/E6010	25.400	28.400	----

---

Table 9 Summary of scenarios

Scenario	Maximum Penetration Depth after 1000 years (cm)			
	Carbon Steel		Cast Iron	
	general	pitting	general	pitting
I	---	---	2.3	9.2
II	---	---	3.6 - 11	8
III	1.9	10.4	0.6	15.2
IV	19 - 28	failure	---	---
V	failure	failure	---	---

Table 10 Typical waste package design work elements

Table 11 Data needed to satisfy design related work elements

Table #10  
TYPICAL WASTE PACKAGE DESIGN WORK ELEMENTS

Determine the conditions that affect waste package design

- ° Thermal Loading
- ° Chemical Environment

Determine the susceptibility of canister materials to degradation

- ° Corrosion
- ° Embrittlement

Determine the release rate of waste forms

- ° Repository Chemical Environment
- ° Repository Thermal Environment

Determine interaction between waste package components

- ° Canister
- ° Waste Form
- ° Backfill

Determine backfill characteristics

- ° Porosity/Permeability
- ° Swelling Properties
- ° Chemical Properties

Table # 11  
DATA NEEDED TO SATISFY DESIGN RELATED WORK ELEMENTS

CHARACTERISTICS OF WASTE PACKAGE COMPONENTS

Physical and chemical properties for:

- ° Waste Form
- ° Canister Materials
- ° Backfill Materials

INTERACTIONS OF COMPONENTS AND NEAR FIELD ENVIRONMENT

- ° Advanced Corrosion Tests
- ° Backfill Performance
- ° Waste Form/Groundwater (Leach)
- ° Basalt/Groundwater (Buffering/Alteration)
- ° Canister/Basalt/Groundwater (Corrosion)
- ° Waste Form/Basalt/Groundwater (Release)
- ° Waste Form/Backfill/Basalt/Groundwater (Retardation Effects)

DESIGN CONCEPTS

- ° Conceptual Design Descriptions
- ° Waste Package Functions
- ° Emplacement Conditions
  - Temperature of Components
  - Groundwater Migration
  - pH and Eh Chemical Composition of Groundwater

Table 12 Waste-package component functions versus repository history for reference waste-package conceptual design

Table 13 Summary of repository conditions in basalt

Table 14 Expected repository conditions at the emplacement location

Table #12

Barrier	Operating Period	Function
Waste form	Preemplacement and repository life	Retard release of radionuclides upon breach of containment
Canister	Preemplacement	Provide physical support and protection of waste form
	Thermal period	Permit retrievability; primary physical barrier to groundwater intrusion
Backfill	Thermal period	Control of water diffusion
	Geologic control	Control of radionuclide diffusion (supports geology)

Table #13

SUMMARY OF REPOSITORY CONDITIONS IN BASALT

	TEMPERATURE (°C)	EQUILIBRIUM pH	E <sub>m</sub> (VOLTS)	PRESSURE (BARS)
OPERATING PERIOD	59	9.6	+0.54	1
THERMAL PERIOD	100	8.7	-0.50	114
	150	7.9	-0.54	114
	200	7.2	-0.57	114
	250	6.7	-0.61	114
	300	6.2	-0.63	114
PERIOD OF GEOLOGIC CONTROL	59	9.6	-0.48	114

Table #14

Expected Repository Conditions at the Emplacement Location.

Period	Condition/operation	Time (yr)	General characteristics (reference horizon)
Preemplacement	Natural undisturbed host rock	0	Low-permeability basalt saturated with alkaline, anoxic water (0.1% by volume) at 59°C hydrostatic pressure.
Containment (thermal)	Construction of waste-emplacement panels	1 to 20	Host rock exposed to atmosphere provided by repository ventilation system.
	Waste emplacement initiated, filled panels isolated from main ventilation system	10 to 80	Basalt heated by the waste package dries the rock in the vicinity of the waste packages. Maximum temperatures reached in emplacement environment.
	Panels, tunnels, and shafts are backfilled and sealed and the repository is decommissioned	80 to 90	Decreased heat-generation rates, as a result of continued radioactive decay, cause lower emplacement-environment temperature. Trapped oxygen being consumed by emplacement media.
	Wastes are contained by the canister	90 to 1,000	Waste-package backfill slowly resaturated, emplacement temperature drops, hydrostatic repository pressure established, and anoxic/alkaline conditions reestablished.
Geologic	Wastes isolated by action of waste form, tailored backfill, repository backfill, and host-rock characteristics	1,000 to 100,000	Repository conditions approach those of original undisturbed host rock.

Figure 1 Pourbaix diagram for (Ref. 6)

Figure 2 Passivation (Ref. 6)

Figure 3 Potential pH diagram for iron  
in high salinity brine at 25 C.

Figure 4 Potential pH diagram  
for iron in high  
salinity brine at 250 C.

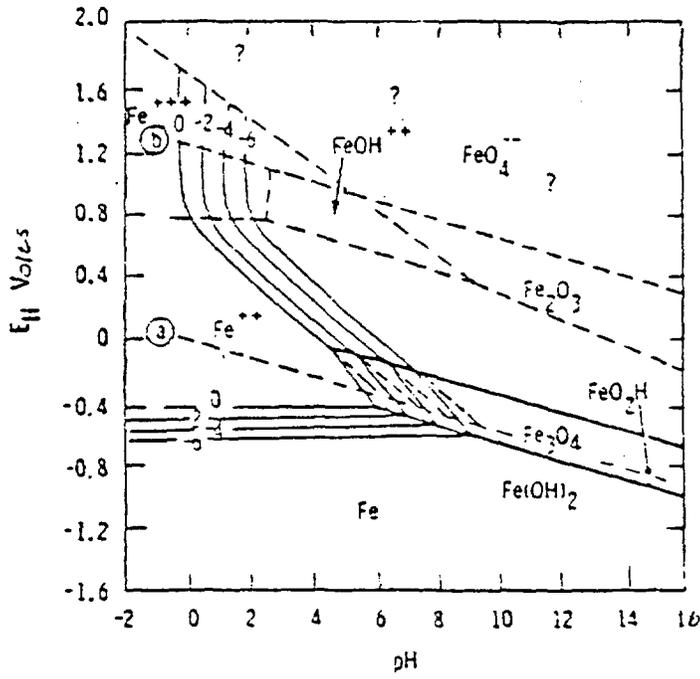


Figure #1 Pourbaix diagram for (6)  
Fe-H<sub>2</sub>O - 25°C

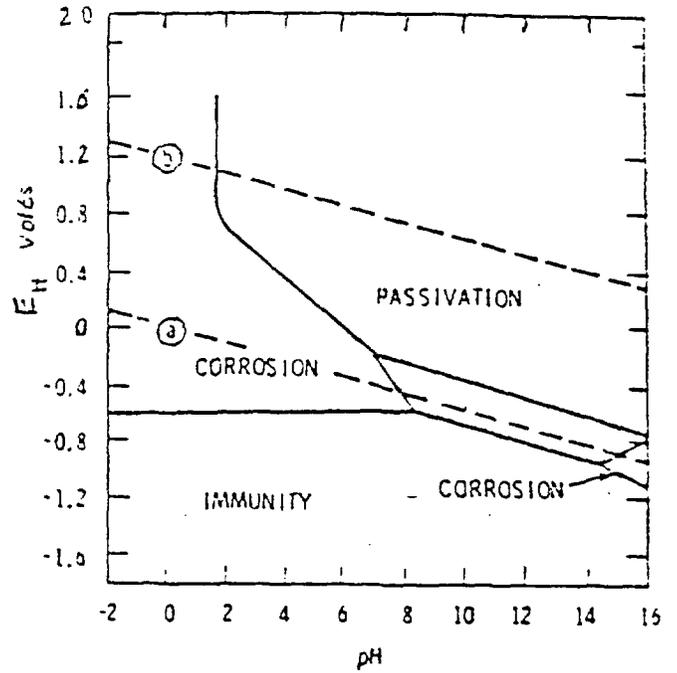


Figure #2 Passivation (6)  
Areas for the Fe-H<sub>2</sub>O System

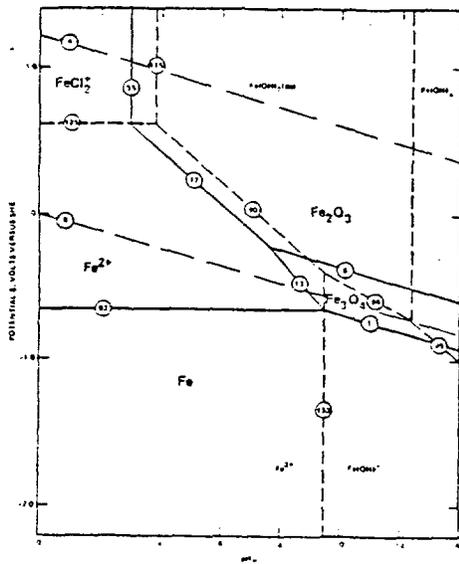


FIGURE 3 - Potential-pH diagram for iron in high salinity brine at 25 C. (7)

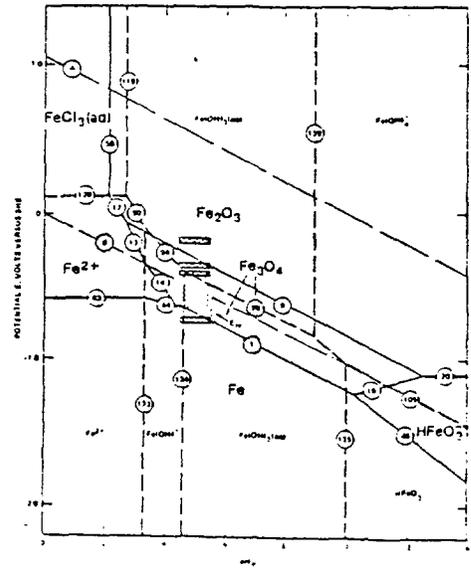


FIGURE 4 - Potential-pH diagram for iron in high salinity brine at 250 C. (7)

- a) represents a lower stability line for water  $H_2 \leftarrow 2H^+ + 2e^-$
- b) represents an upper stability line for water  $H_2O \rightarrow 1/2 O_2 + 2H^+ + 2e^-$

Figure 5 Corrosion of gray iron in soils of differing resistivity

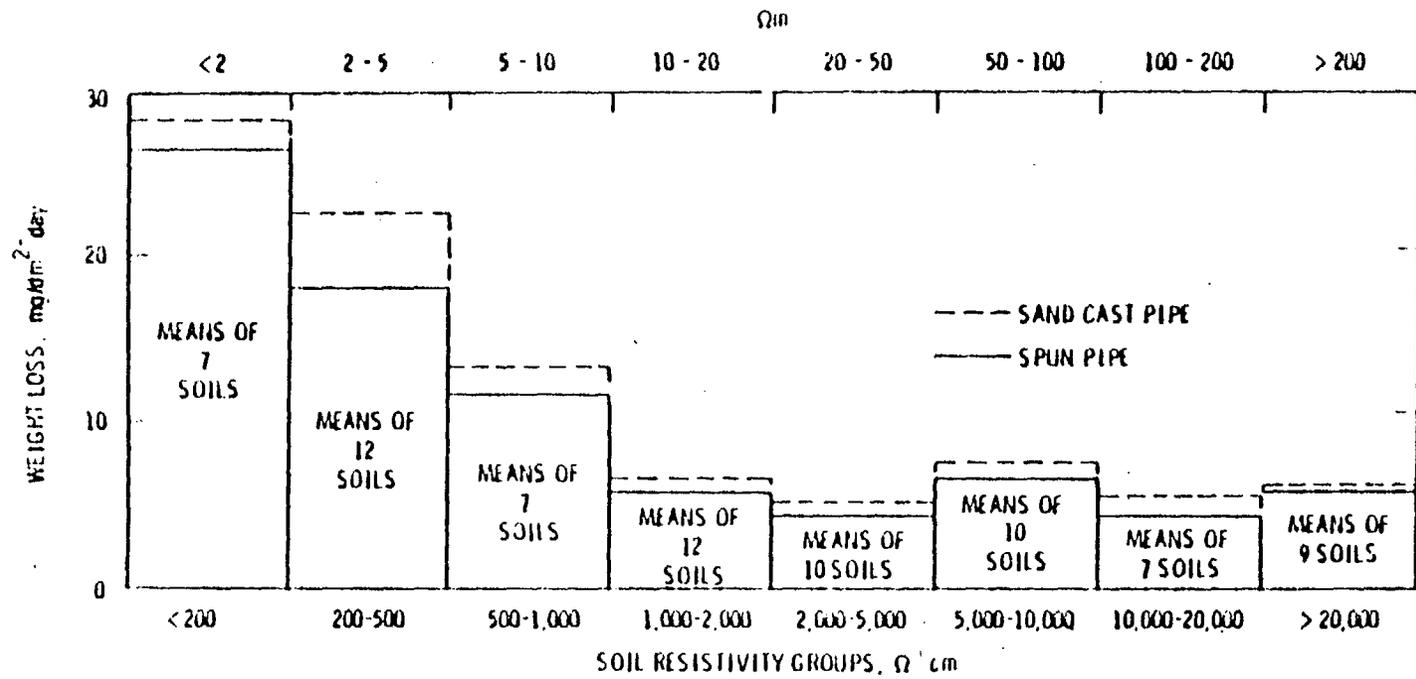


FIGURE 5. Corrosion of Gray Iron in Soils of Differing Resistivity

Figure 6 Pourbaix diagram for iron with 355 ppm  $\text{Cl}^-$

At pH 8 this can be interpreted as: (Ref. 6)

- 1 = general corrosion of nonpolarized iron in anoxic solution.
- 2 = pitting of nonpolarized iron in oxic solution.
- 3 = active pits or crevices.

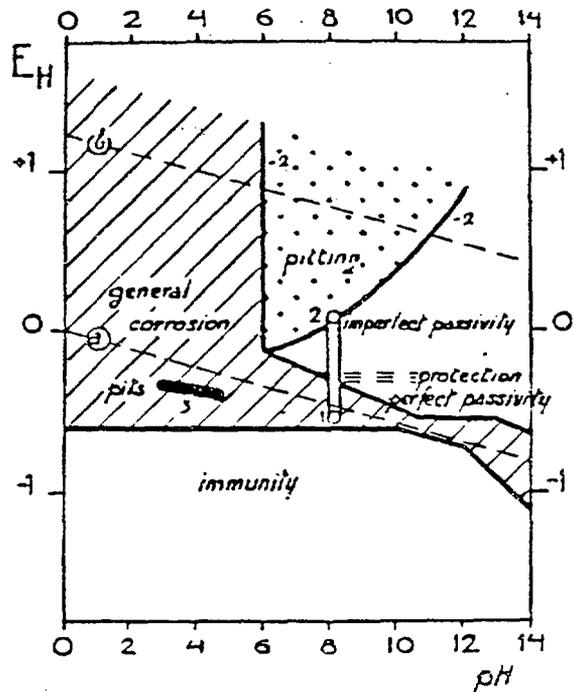


Figure #6 Pourbaix diagram for iron with 355 ppm Cl<sup>-</sup>

At pH 8 this can be interpreted as: (6)

- 1 = general corrosion of nonpolarized iron in anoxic solution.
- 2 = pitting of nonpolarized iron in oxidic solution.
- 3 = active pits or crevices.

Table #7 Basalt Groundwater (4)

<u>Ion</u>	<u>Concentration (ppm)</u>	<u>Millequivalents</u>
Na <sup>+</sup>	250	10.870
K <sup>+</sup>	1.9	.050
Mg <sup>2+</sup>	0.04	.004
Ca <sup>2+</sup>	1.3	.066
CO <sup>-2</sup>	27	.900
HCO <sub>3</sub> <sup>-</sup>	70	1.148
OH	1.4	.082
H <sub>3</sub> SiO <sub>4</sub>	103	1.084
Cl <sup>-</sup>	148	1.096
SO <sup>-2</sup>	108	2.250
F <sup>-</sup>	37	2.176

Figure 7 Dimensions of a repository draft

Figure 8 Typical crosssection of repository

Figure 9 Dimensions of boreholes between drifts

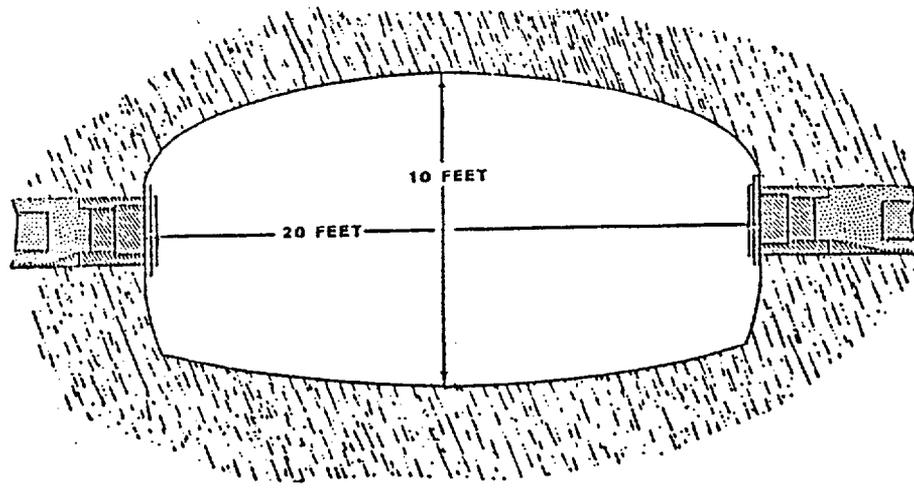


Figure #7 Dimensions of a Repository Drift

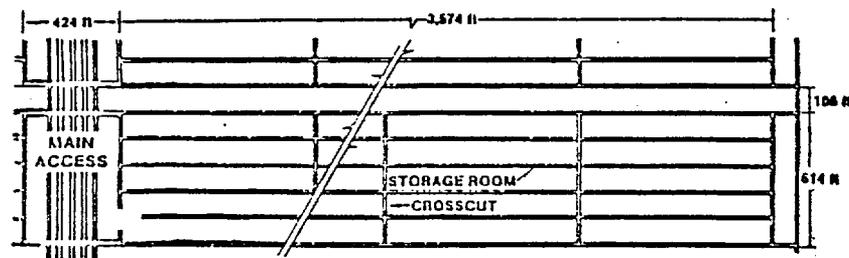
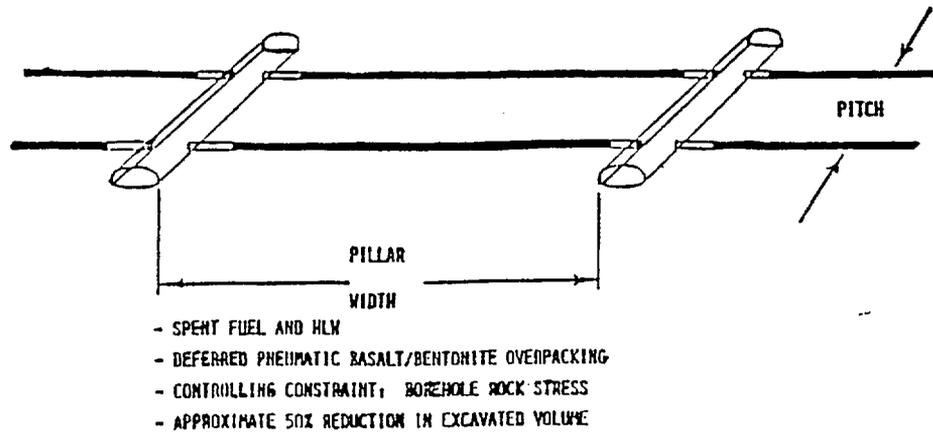


Figure #8 Typical Crosssection of Repository



Fig#9 Dimensions of Boreholes between Drifts

Figure 10 Borehole design

Figure 11 Backfilling Main Shaft of Repository

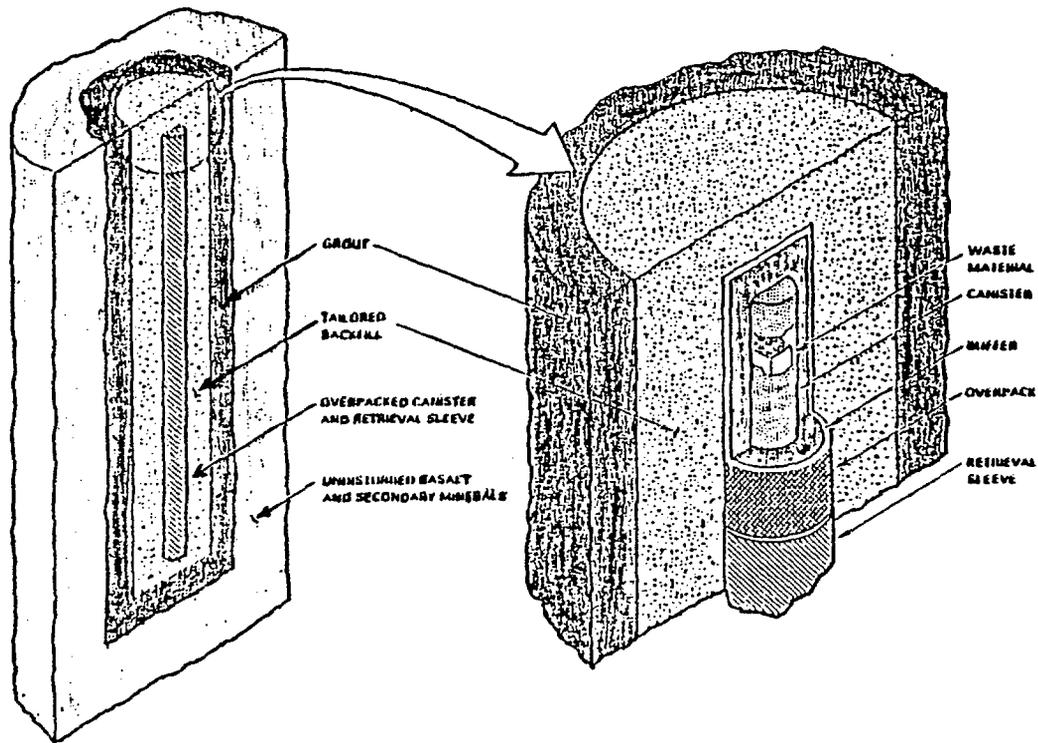


Figure #10 Borehole design

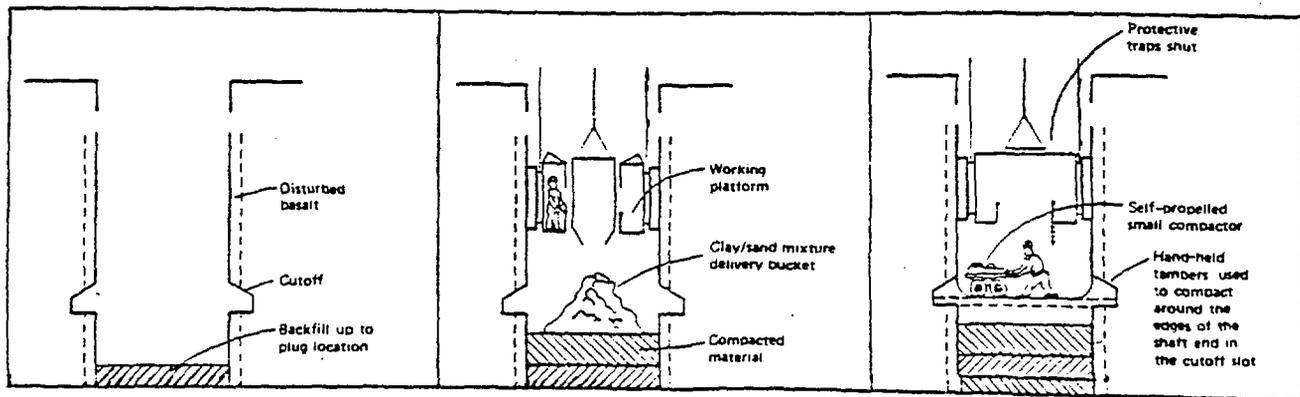


Figure #11 Backfilling Main Shaft of Repository

Figure 12 Backfilling of borehole

Figure 13 Backfilling a large drift

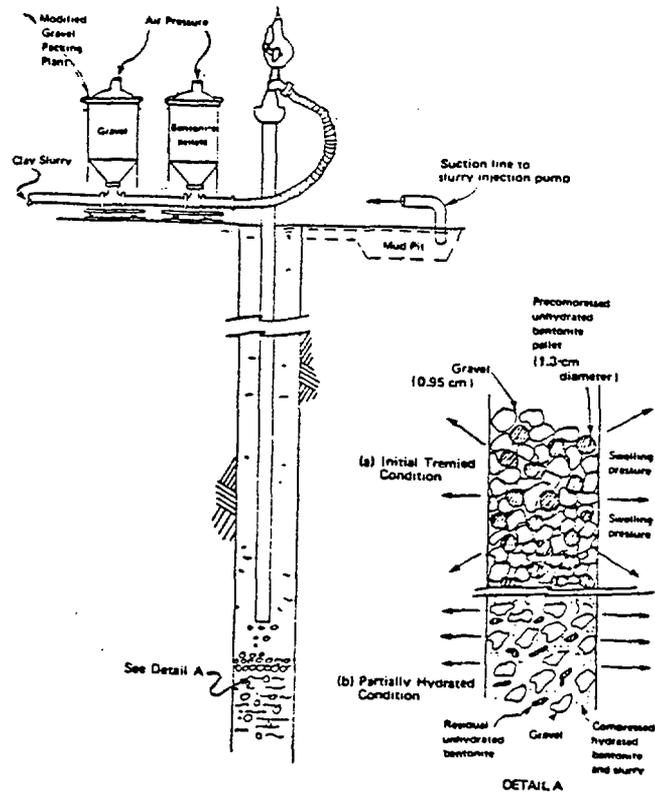


Figure #12 Backfilling of Borehole

note: This design assumes vertical borehole

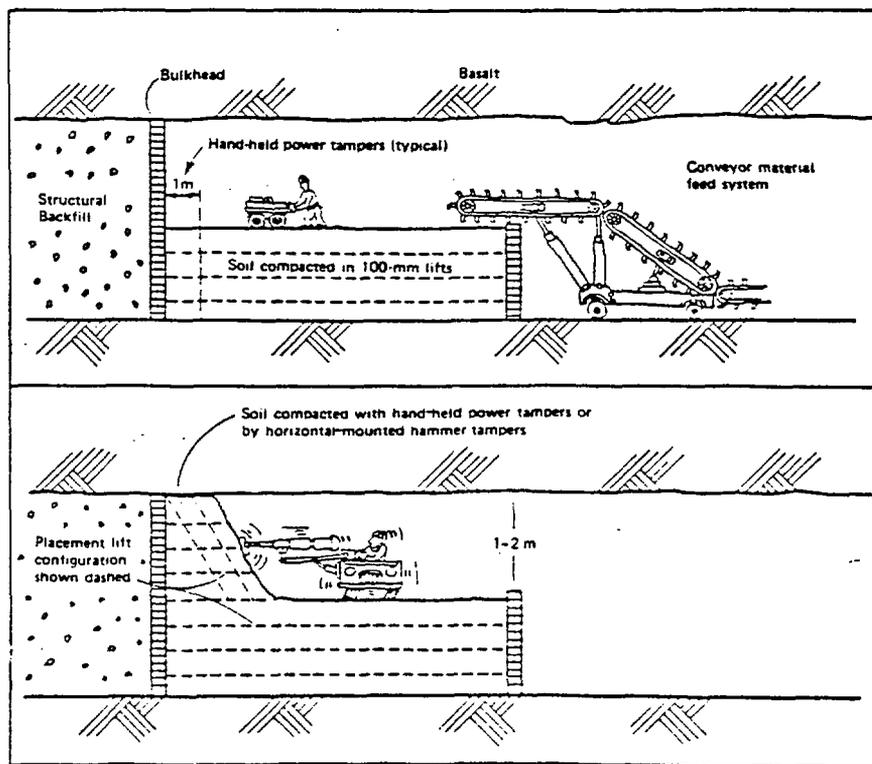


Figure #13 Backfilling a large Drift

Figure 14 Canister construction with dimensions

Figure 15 Canister emplacement

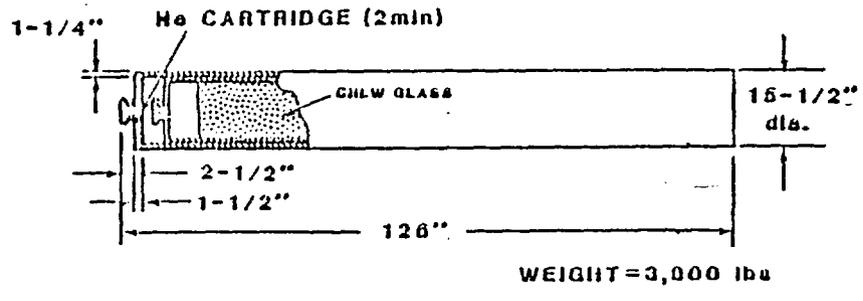
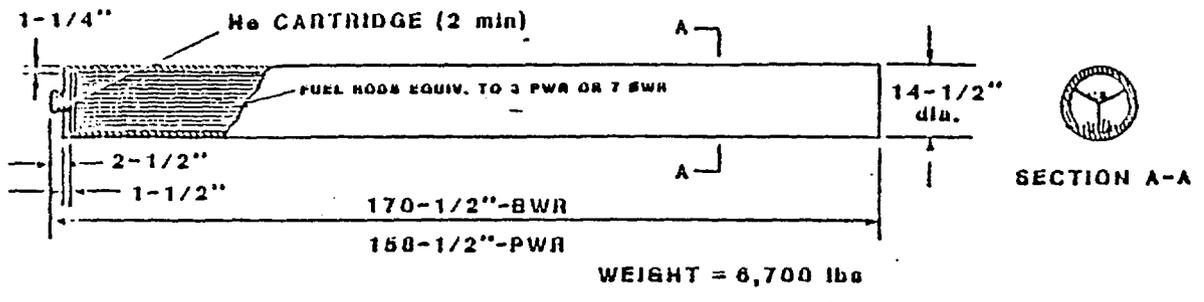


Fig. #14 Canister Construction with Dimensions

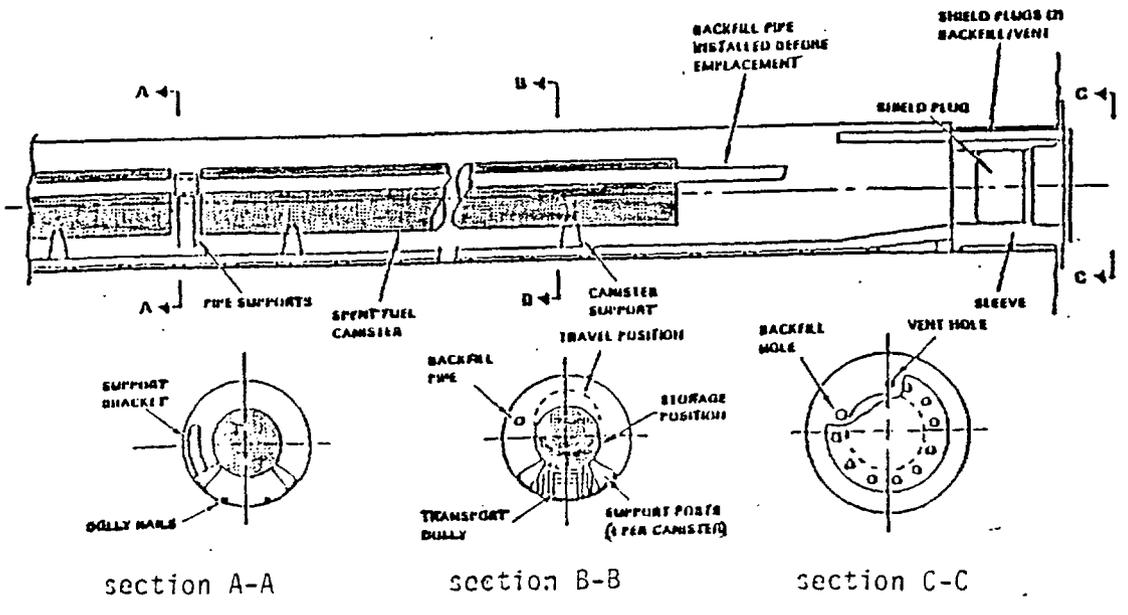


Figure #15 Canister emplacement

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APPENDIX Q  
DEGRADATION MECHANISMS OF BOROSILICATE GLASS

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## 1. INTRODUCTION

The predominant effort in the development of a waste form for the containment of radioactive waste is encapsulation in glass.

Glass in contact with water is a "worst case" scenario that assumes nuclear waste repository flooding in which the glass will be subjected to various types of chemical and mechanical damage. The main thrust in waste form development centers on the performance of the waste form as a barrier to radionuclide release. A thorough understanding of the physical and chemical properties of the waste form as well as its probable behavior in a variety of aqueous environments are prerequisites to the assessment of waste form integrity over geological time.

Given the lack of any existing comprehensive reviews, the purpose of this report is to outline the mechanisms of glass corrosion under various laboratory and field conditions through a compilation of current data. Emphasis is given to commercial and nuclear waste borosilicate glasses since these are the primary candidate compositions for nuclear waste encapsulation. The data presented will be relevant to either a direct loading of waste in a glass matrix or to a waste form design utilizing sacrificial glass layers. Other glass types are included for the purpose of comparison and for those instances where these tend to illustrate various processes of glass corrosion common to all glass compositions. Within each section of the report, processes are discussed pertinent to any attempt at long-term prediction of glass corrosion.

The inherent radiation environment of the nuclear waste package is another factor to be considered for the assessment of the integrity of glassy waste forms. A brief summary of the radiation effect and its consequences are also presented.

Since data on most of the processes discussed in the text are not currently available, solubility and leaching data for commercial and waste borosilicate glasses are presented as a separate appendix to this report.

This review will form the basis of our evaluation of glassy and alternative waste forms in BNL's waste package overview and test development tasks for the NRC's Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria.

## 2. GENERAL CORROSION

General corrosion is a major mode of leaching in glass. In the discussion that follows we will first summarize the models for dissolution kinetics and corrosion mechanisms. More specifically, the solution effects and the effects of various glass characteristics are critically evaluated for commercial and nuclear waste borosilicate glass. The variables under consideration in evaluating solution effects include solution composition, pH, flow rate, temperature, pressure, and reprecipitation. The discussion of glass characteristics includes composition, phase separation, surface area to volume ratio, surface stress, cracks, surface finish, and matrix inhomogeneity.

Cation selectivity in ion exchange and diffusion of gas and ions are reviewed separately since both characteristics are important to the assessment of radioisotope migration and gas generation over geologic time. Finally, consideration is given to corrosion by weathering particularly by the vapor phase since this is likely condition to be encountered in actual repository environments.

### 2.1 Kinetic Law

There is general consensus that in a static condition stage 1, dealkalization reactions occur with a square root time dependence at low to intermediate pH values while the appearance of a stage 2, network dissolution reaction occurs with a linear time dependence at high pH. The fractional power relation between the amount of alkali removed  $Q$  and the time  $t$ , therefore, may be expressed in the form:

$$Q = a\sqrt{t} + bt \quad (1)$$

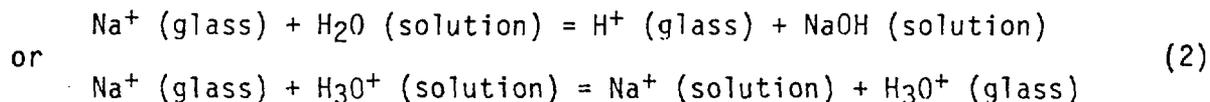
where  $a$  and  $b$  are appropriate constants. No comprehensive mechanistic studies are available at the present time to explain this relation. The square root indicates a diffusion controlled reaction and the linear relation reflects an interface controlled reaction. The relation is more or less empirical in nature. Most of the experiments are reconcilable with an overall rate process which varies with ' $t$ ' at short times and low temperatures, and ' $t^2$ ' at long times and high temperatures. Examples include the work done by Berger<sup>(1)</sup> on glass powders, by Douglas and El-Shamy<sup>(2,3)</sup> on alkali-oxide silica and soda-lime silica glasses, and by PNL<sup>(4)</sup> on PNL 72-68 glass.

Although there has been considerable controversy over the transition between the square root to linear time regimes, as well as in the extent of the transition and the origin of it, it is generally acknowledged that the change from diffusion controlled stage 1 to interface controlled stage 2 primarily depends on the time required for the pH to reach a value of 9-10. It has been observed that the long transition period occurs only when glass powders are corroded. In powdered glass, concentration-cell effects locally increase the surface-area-to-volume ratios causing a rapid increase in the pH surrounding many of the glass particles.

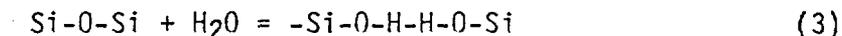
The formulation of leach kinetics through the use of empirical or semi-empirical equations is based on several assumptions such as homogeneous leaching, the preservation of leachant composition, surface area and mechanical integrity. In real situations, these factors should be incorporated into the formulations.

## 2.2 Reaction Mechanism and Kinetic Models

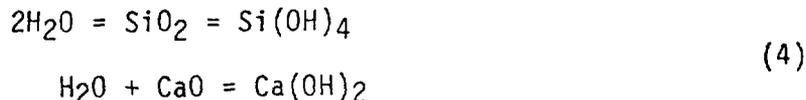
At least three different stages are involved in the reaction of water with a silicate glass containing alkali ions: The first is ion exchange of hydronium ( $H_3O^+$ ) or hydrogen ions from the water with alkali ions in the glass; the second is the partial hydration of the silicon-oxygen network of the glass; and the third is the dissolution of the glass into the contacting solution. Either or both of the first two steps can be absent, depending upon glass composition or solution pH, and the third is absent when the glass reacts with water vapor instead of liquid water or a solution. The initial exchange of alkali ions in the glass and hydrogen or hydronium ions from water can be described<sup>(5,6)</sup> as follows:



In this layer of partial exchange the network structure of the glass is intact and the only change is the replacement of one ion by another. Closer to the glass surface the network can become partially hydrated through the reaction of silicon-oxygen bonds with water:<sup>(5)</sup>



This partial hydration leads to a more open structure than in the original glass; ions from solution and water molecules can penetrate through this partially hydrated or gel layer with mobilities much higher than in the glass network which remains intact. At extended times of reaction, silicon and other glass constituents dissolve as follows:<sup>(5)</sup>



The dissolved species are ionized further. Sometimes, hydration involves stress generation in the hydrated layer causing swelling, contraction, cracking or peeling of the layer.

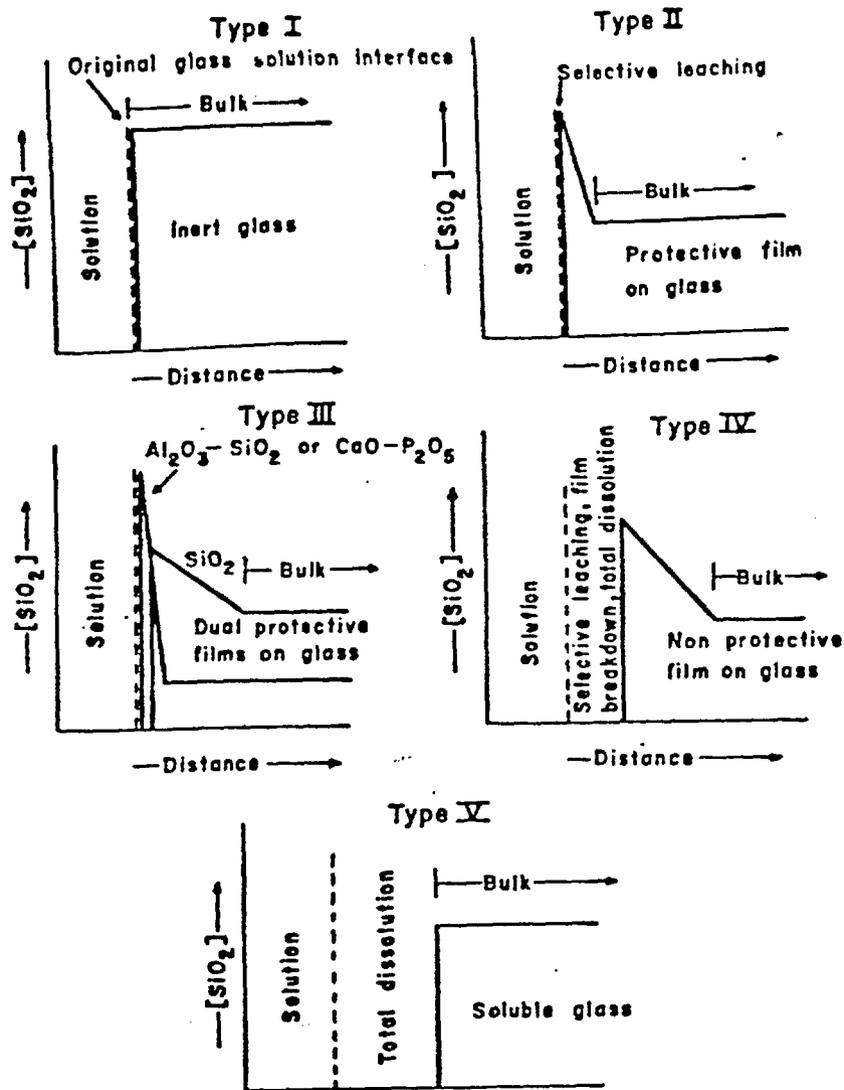


Figure 2.1 Five types of surfaces developed during the leaching of silicate glasses. (7,8)

In more complicated systems, the absence of one or more steps described above leads to another classification of corrosion modes in view of the apparent overall dissolution. The glass may: (1) react with the corrosive materials to form new compounds on the surface; (2) be preferentially dissolved leaving a leached surface layer; (3) be totally dissolved continuously exposing fresh glass. Workers at the University of Florida<sup>(7,8)</sup> extended this concept to five types of surfaces (Figure 2.1) of a silicate glass and correlated these to its durability. A type I surface has undergone only a thin,  $<50\text{\AA}$ , surface layer hydration. Vitreous silica exposed to neutral pH solutions has a type I surface. A type II surface possesses a silica-rich protective film due to selective alkali ion removal. A glass with this type of surface is reasonably durable. Two layers of protective surface films are characteristic of type III. Such glasses are very durable in both acid and alkali solutions. Type IV glass surfaces also have a silica-rich film but the silica concentration is insufficient to protect the glass from rapid attack by dealcalization of network dissolution, resulting in poor durability. A glass of type V undergoes uniform attack losing considerable quantities of ions into solution.

A. Paul<sup>(9)</sup> proposed the importance of the thermodynamic stability as well as conventionally studied kinetic stability. The relative influence of either of these two factors on durability will depend on the nature of the test. For low temperature tests, the kinetic aspects will be predominant while thermodynamic considerations will be more important if the surface area of the glass sample exposed to the corroding medium is high, and/or the experiment is carried out at relatively high temperatures. Also, it is very likely that steady potentials will be obtained with conventional glass electrodes within a short time such that the kinetic barrier would not appear to play any important role, at least at the surface of the glass. Paul calculated the stability of different oxides commonly used in glass making ( $\text{SiO}_2$ ,  $\text{ZnO}$ ,  $\text{PbO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , etc.) in aqueous solutions at different pH, and related the quantitative results to the corrosion behavior of various glass compositions. The important finding of this study is that the long-term chemical resistance of a glass may be determined by the thermodynamic activity and stability of its component oxides in aqueous solutions.

A quantitative prediction and interpretation of glass durability as a function of time needs comprehensive analytical models based on the qualitative and mechanistic observations described above. Doremus<sup>(5)</sup> proposed a mathematical model in which the two steps of interdiffusion of ions and dissolution of the glass can be combined in a diffusion model where the surface of the glass is progressively removed. By solving the diffusion equations of a moving boundary, the model estimates the kinetics of the cumulative amount  $Q$  of ions diffusing out of the glass per unit area; square root of time law at early stages, linear time law at longer periods for a diffusion coefficient independent of composition, and approximately linear time law at longer times for a concentration-dependent diffusion coefficient. Obviously this model is oversimplified considering the many factors involved during the corrosion process such as changes in solution chemistry as well as various glass characteristics which will be discussed separately in later sections. In spite of the

simplification, the study presents important features in the long-term prediction of glass durability. As the corrosion system becomes complicated as in the case of a concentration-dependent diffusion coefficient, the kinetic equations will also be complicated. During the laboratory testing period, the kinetics can be approximated by a linear time law. However, for longer time extrapolation, the exact solution may exhibit significant discrepancy from the linear behavior. Thus, it may not be valid to use the simple apparent linear time law in the prediction of long-term glass durability. Also, the authors have found that even in a simple system it is necessary to make measurements over a range at least three to four orders of magnitude in time to obtain reliable values for the coefficients of  $\sqrt{t}$  and  $t$  of the kinetics, since it is easy to deceive oneself about the linearity of the plots of  $Q$  against  $t$  or  $\sqrt{t}$ . The interpretation of short-term laboratory data should take these facts into account.

A similar model was proposed by Godbee et al. (10,11) based on mass transport theory which assumes that diffusion through the solid is a rate-limiting process. They include factors arising from more complicated situation such as periodic leachant renewal, initial wash-off of active or contaminated surface, the rapid change of surface concentration as well as the moving boundary condition by surface dissolution. The calculated results show good agreement with the cumulative loss of radioactive isotopes leached by distilled water from waste borosilicate glass and cement. Similar models have been developed by Ewest, (12) for more ideal situations, and by Machiels, (13,14) including surface reaction and diffusion processes. Again it is pointed out that data fitting based on short-term laboratory tests may result in significant discrepancies when such models are applied to long-term predictions.

Workers at Catholic University of America (15-18) have attempted to calculate the cumulative mass release from the waste form over geologic time based on experimentally observed corrosion rates of glass. This model is the first attempt to include the flow conditions and the accompanying pH change of the leachate. The model is purely phenomenological in its assessment of leach rates in that it lacks a basic understanding of the corrosion mechanisms.

At the present time, more comprehensive models that would take into account the complex factors involved in real corrosion systems are not available for estimating glass durability. Due to a lack of basic data, it is perhaps too premature to attempt a complete formulation of corrosion kinetics for glass.

## 2.3 Solution Effects

### 2.3.1 Solution Composition

A small concentration of ions present in water or other aqueous solutions affects glass leachability in various ways. Preliminary studies by Hench, et

al.(19) have shown that leach rates in groundwater are greatly decreased from those in deionized water commonly used in laboratory experiments. During the leaching process, the pure solution will undergo compositional change as the rate of surface attack progresses until it reaches a steady-state value; concomitantly the solution will contain some fraction of the ions from the glass components. A significant fraction of the mixed alkali effect, for example, is due to solution ion effects (Mixed alkali effect: If a second alkali oxide, such as potassium, is added to a sodium silicate glass, the durability of the glass is increased; the presence of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  together serves to lower the rate of surface dealcalization).

The influence of the salt compounds in improving durability has been investigated, indicating some of the effects of solution ions on the durability of glass.(4,7) The influence of the salt compounds on leaching are in decreasing order:  $\text{CaCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{AlCl}_3$ . Two extremes,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , will be described as follows:  $\text{Ca}^{2+}$  ions in solution improve the corrosion resistance of binary alkali-silicate glasses by a factor of 10 in comparison with pure water; for  $\text{Al}^{3+}$  ions (<25 ppm), glass dissolution increased due to a more rapid increase in dealcalization and resultant solution pH. This is due to insufficient  $\text{Al}^{3+}$  ions to passivate active surface sites and incomplete formation of stable alumino-silicate surface complexes. At concentrations greater than 25 ppm  $\text{Al}^{3+}$ , the total dissolution of the glass is greatly reduced. Sufficient concentration of  $\text{Al}^{3+}$  in solution creates a dual protective film against extensive network dissolution. The rate of selective leaching or ion exchange is relatively unaffected by the presence of  $\text{Al}^{3+}$  in solution.

In brine solutions, the leach rates of waste glass are generally lower than in DI water and silicate water.(20) Alkaline elements released will enhance the durability because of resultant salinity increases. Cs and Mg, however, have an adverse effect. These changes, though, are well within an order of magnitude. Limited data exist on the effects of anions and organics in leachants. The oxidation potential (Eh) is also controlled by the small concentrations of the ions present in solution. For all practical purposes, Eh effects would tend to be insignificant under repository conditions.

### 2.3.2 Solution pH

There is a fundamental difference between chemical attack by water or acids and that of alkaline solutions. The former limit their action to the other constituents but have very little effect on silica, while the latter attacks all constituents, including silica. The general effect of pH of the solution on the relative rate of attack for a low expansion borosilicate glass is shown in Figure 2.2. The test was performed at a temperature of 95°C. Figure 2.3 shows the rate of attack for a borosilicate glass (Corning 7740) in 5% NaOH at 95°C. Below pH 7, alkali or alkaline earth ions are replaced by hydrogen or hydronium ions, but the silica matrix of the glass is unaffected. As the solution becomes more alkaline, the silicic acid formed by bulk

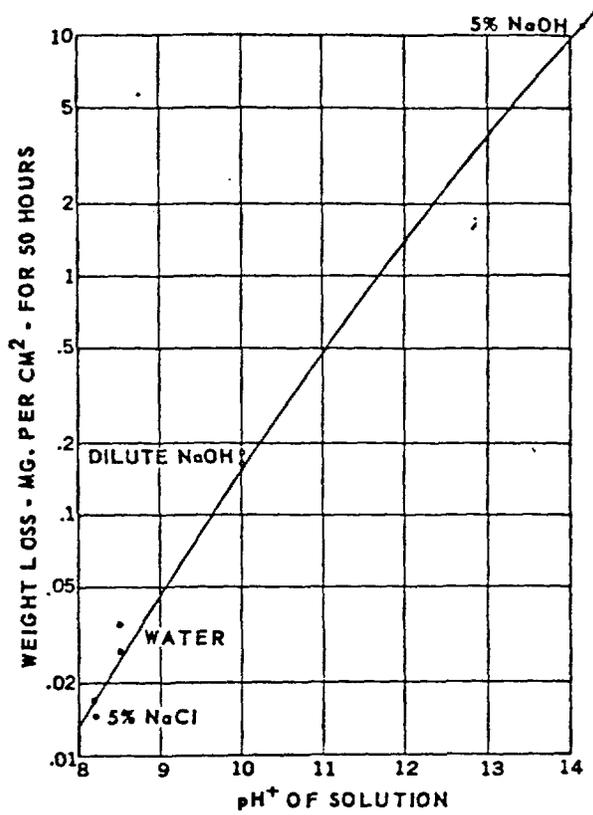


Figure 2.2 Durability of low-expansion borosilicate glass vs pH of the reagent at a temperature of 95°C. (21)

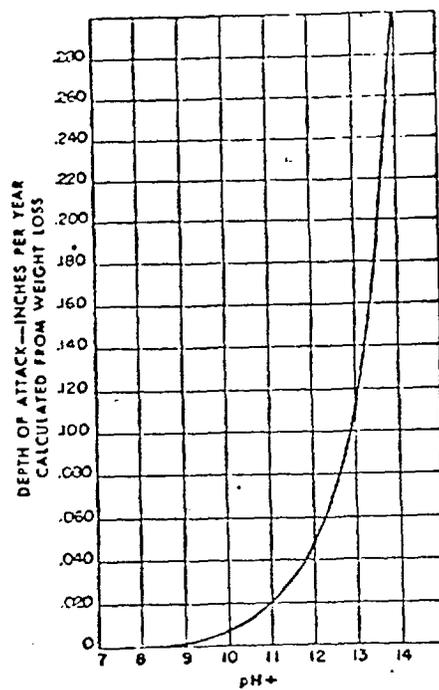


Figure 2.3 Rate of attack on Corning 7740 in 5% NaOH at 95°C. (22)

bulk amorphous silica in water ionizes and dissolution becomes more rapid. Because of the ionization reactions, the solubility of amorphous silica increases sharply above a pH of about 9, leading to a sharp increase of the dissolution rate above this value. The dissolution of silicate glasses, therefore, shows a strong dependency on the solution pH. The dissolution rate is not influenced much by pH in neutral or acidic solutions because the dissolving species (non-ionized silicic acid) has a nearly constant solubility. In a static leaching condition, a transition occurs by the replacement of alkali ions to increase silica dissolution. Hench<sup>(19)</sup> explained this transition in terms of typical surface structures (see Fig. 2.1); the change from a protective surface (type III) to a rapidly deteriorating surface (type IV or type V).

El-Shamy et al.<sup>(23)</sup> presented experimental data on the dependence on pH of the decomposition for a number of alkali oxide-silica and soda-lime-silica glasses. Typical examples are shown in Figures 2.4 and 2.5. Sodium extraction is indicated for S15 glass; silica removal is shown for P15 glass.

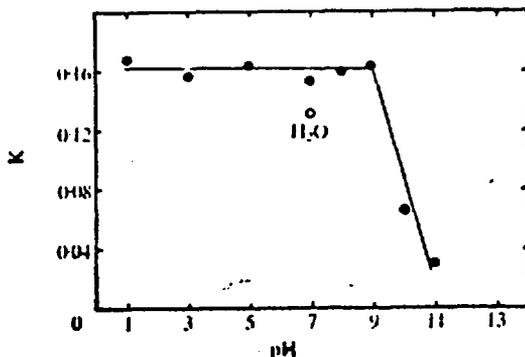


Figure 2.4 Dependence upon pH of the rate of extraction of sodium oxide  $[mg\ g\text{-glass}^{-1}\ (\sqrt{\text{min}})^{-1}]$  from S15 glass at 35°C.<sup>(23)</sup>

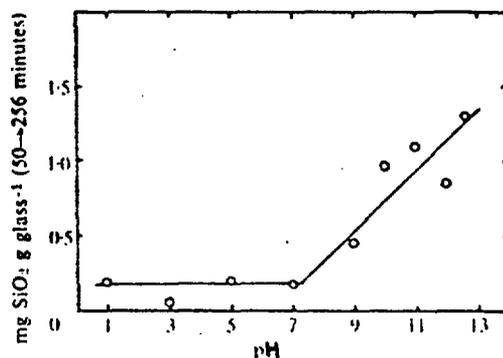


Figure 2.5 Dependence upon pH of the removal of silica from P15 glass at 35°C.<sup>(23)</sup>

The addition of other constituents, such as lime, only slightly modified the typical shapes of the graphs. For more complicated commercial glasses, this general trend may still be valid with some modifications for the addition of multicomponents. The quantitative and detailed effects of these multicomponents are not known at the present time. Some examples are given below.

In alkaline solutions, boron oxide in Pyrex borosilicate glass does not influence, to any great extent, the rate of dissolution of the silicate lattice, while in some instances (7050 glass) it leads to reduced alkaline durability. Similarly, in 0010 glass a small amount of lead has little effect on durability, while in larger concentrations it reduces alkaline durability.

Certain ions in the glass can lead to preferential attack by acid solutions. Glasses containing substantial amounts of boron, aluminum, or lead, such as Corning 1720 and 7050, are much more rapidly attacked by acid than soda-lime glass, while Pyrex and vitreous silica glasses retain their durability. The high solubilities of boron, aluminum, and lead oxides in acid apparently lead to their deleterious influence on the durability of glass.

Such complications lead to the unexplainable pH dependence on the leach rates of U.K. borosilicate waste glass as shown in Figure 2.6<sup>(24)</sup>. It can be seen that the leach rates are increased by low pH leachants. At high pH the leach rates are also increased. Similar results were also obtained for Savannah River Plant (SRP) borosilicate waste glass covering a wider range of pH than the U.K. study. The SRP results are shown in Figure 2.7 and 2.8.<sup>(25,26)</sup>

Waste glasses usually contain less than 50 wt.%  $\text{SiO}_2$  while commercial container glasses contain more than 70 wt.%  $\text{SiO}_2$ . This accounts for the difference in behavior at lower pH.<sup>(27)</sup> At high pH, the trend of leach rates generally follows that of commercial glasses. In actual repository conditions, the unbuffered solution would have little effect on the leach rate while a buffered solution may change the leach rates significantly as a result of the pH shift.

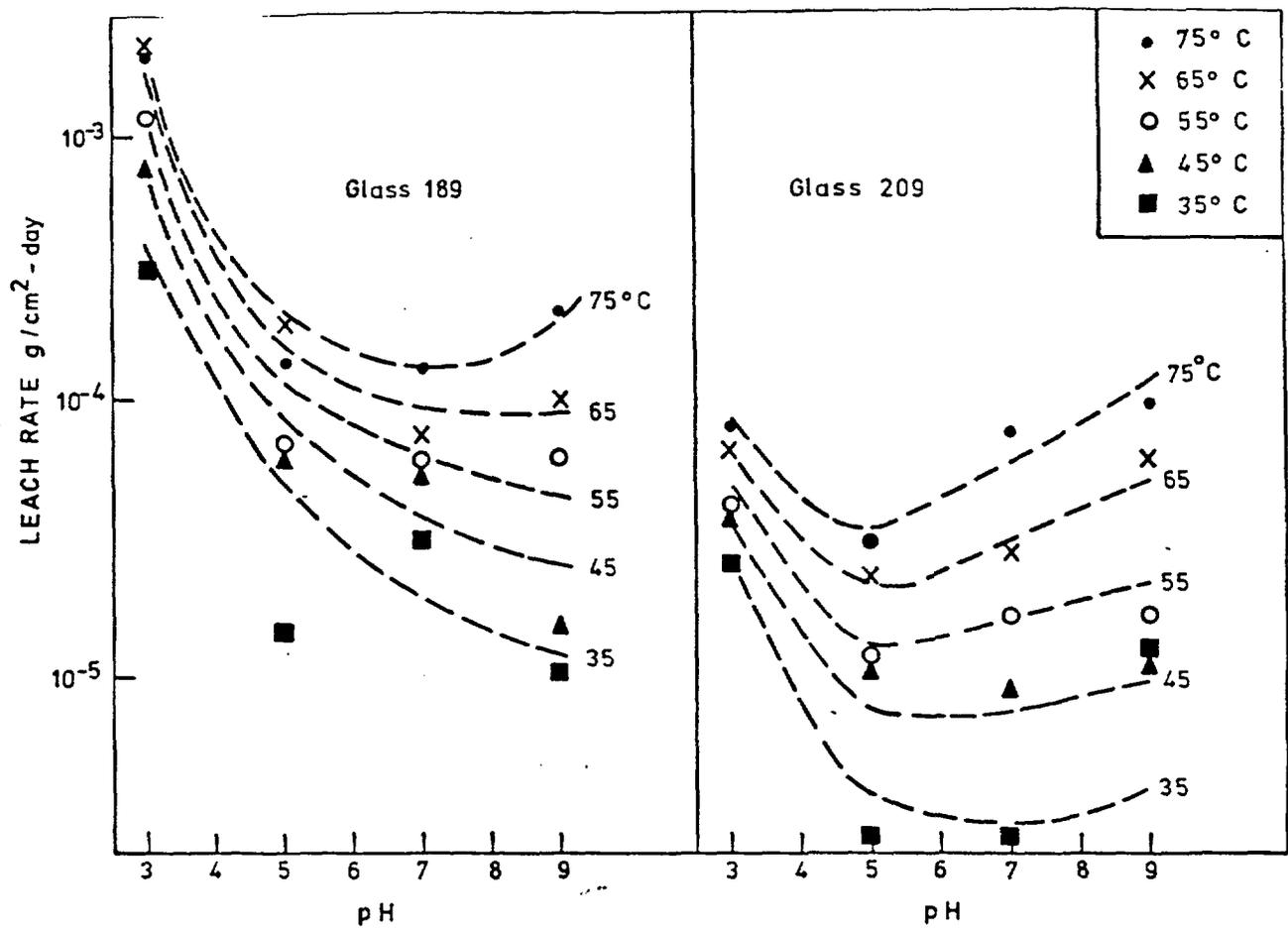


Figure 2.6 The effect of pH on the leach rate of glasses 189 and 209 at different temperatures. (24)

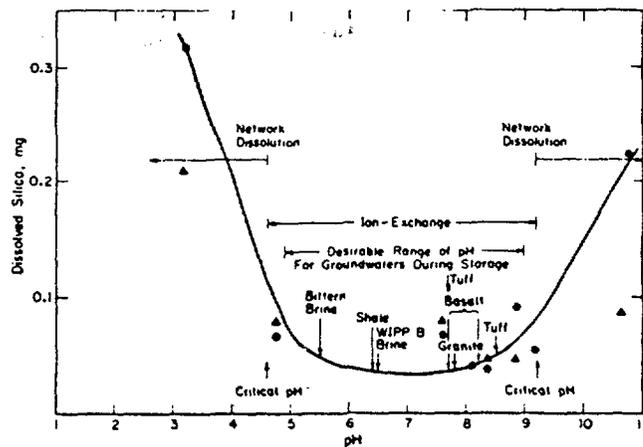


Figure 2.7 Silica dissolution vs pH curve of SRP glass. (25)

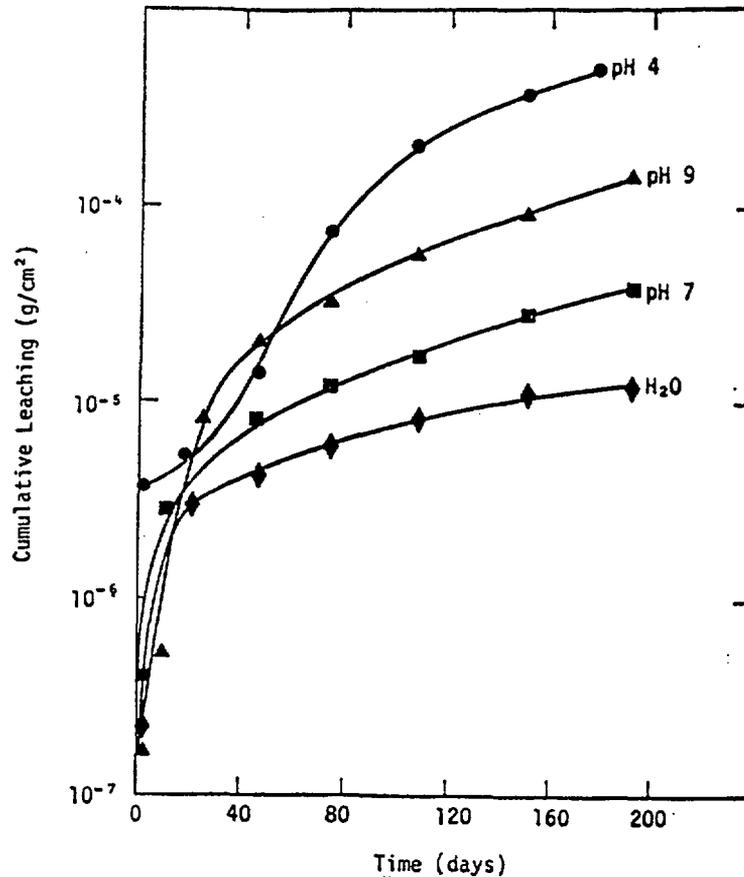


Figure 2.8 Cumulative leaching based on <sup>90</sup>Sr analysis of SRP glass.(26)

### 2.3.3 Flow Rate

The replenishment or flow of solutions has been reported as showing two opposite effects on the glass corrosion. In a leach test of K<sub>2</sub>O-SiO<sub>2</sub> glass at 40°C(3), a marked increase in the extraction of silica was shown as the number of replenishments is decreased. The increase can be attributed to the evident accompanying rise in the pH of the attacking solution. If the flow rate is slower than the rate of replenishment, the dissolution rates will slow down as a result of the saturation of the surrounding medium by silica.(17) If the flow rate is high enough to keep the system from leaching saturation, this could account for conditions exhibiting higher leach rates. However, should reprecipitation of insoluble hydroxides, hydrates oxides, or silicates at high pH occur, radionuclide release to the environment could be saturated.(28) At very high flow rates, the leach rates would be controlled by the pH of the medium and the stability of the dealcalized layer. Taylor and Smith(21) reported a significant increase in weight loss under these erosive conditions.

Some leach data are available for the behavior of waste borosilicate glass subjected to different flow rates. Leach rates on British waste glasses<sup>(24)</sup> were obtained using a Soxhlet apparatus, heating in static water, and exposed to flowing ( $1 \times 10^{-8}$  m<sup>3</sup>/sec) water. Duration of the tests was dependent on time sufficient to achieve a measurable weight loss. This varied from approximately one week at 100°C to several months at ambient temperature. Leach rates were obtained (Figures 2.9 and 2.10) over a range of temperatures. The figures point to higher leach rates in the Soxhlet method over the static. Glass 189 was doped with 5 weight percent <sup>238</sup>Pu and stored. The results obtained in Soxhlet leach tests for yearly intervals are shown in Table 2.1. It is evident that higher leach rates are obtained using the Soxhlet method than in static tests. Under repository conditions, the slow flow rates would tend to have an insignificant affect on the leach rates as indicated by the above observations.

Table 2.1

Results of Soxhlet Tests of U.K. Glass for Yearly Intervals<sup>(24)</sup>

Temperature (C°)		Total Dose Over 3 yrs Disintegra- tions per g	Leach Rates, (g/cm <sup>2</sup> -day) at 100°C		
First yr	Subsequent yrs		After 1 yr	After 2 yrs	After 3 yrs
50	20	$2.7 \times 10^{18}$	$1.6 \times 10^{-3}$	$2.3 \times 10^{-3}$ $2.4 \times 10^{-3}$	$2.3 \times 10^{-3}$
170	20	$2.7 \times 10^{18}$	$1.5 \times 10^{-3}$	$2.3 \times 10^{-3}$ $2.2 \times 10^{-3}$	$2.6 \times 10^{-3}$

A-14

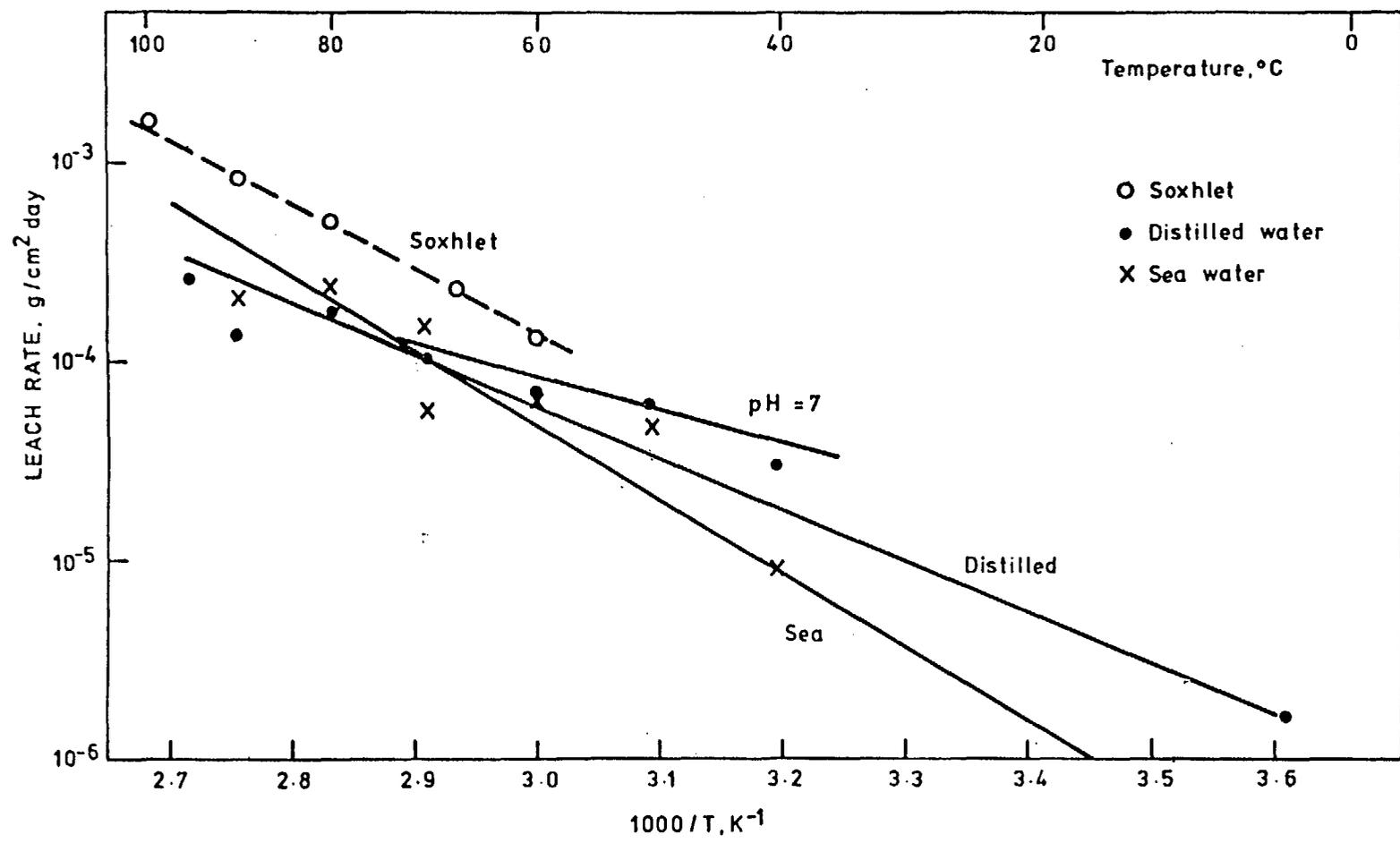


Figure 2.9 Soxhlet and static water leach rates for glass 189. The Soxhlet results for temperatures below 100°C were obtained by boiling the water under reduced pressure. The leach rates in flowing water (pH=7) are included for comparison. (24)

A-15

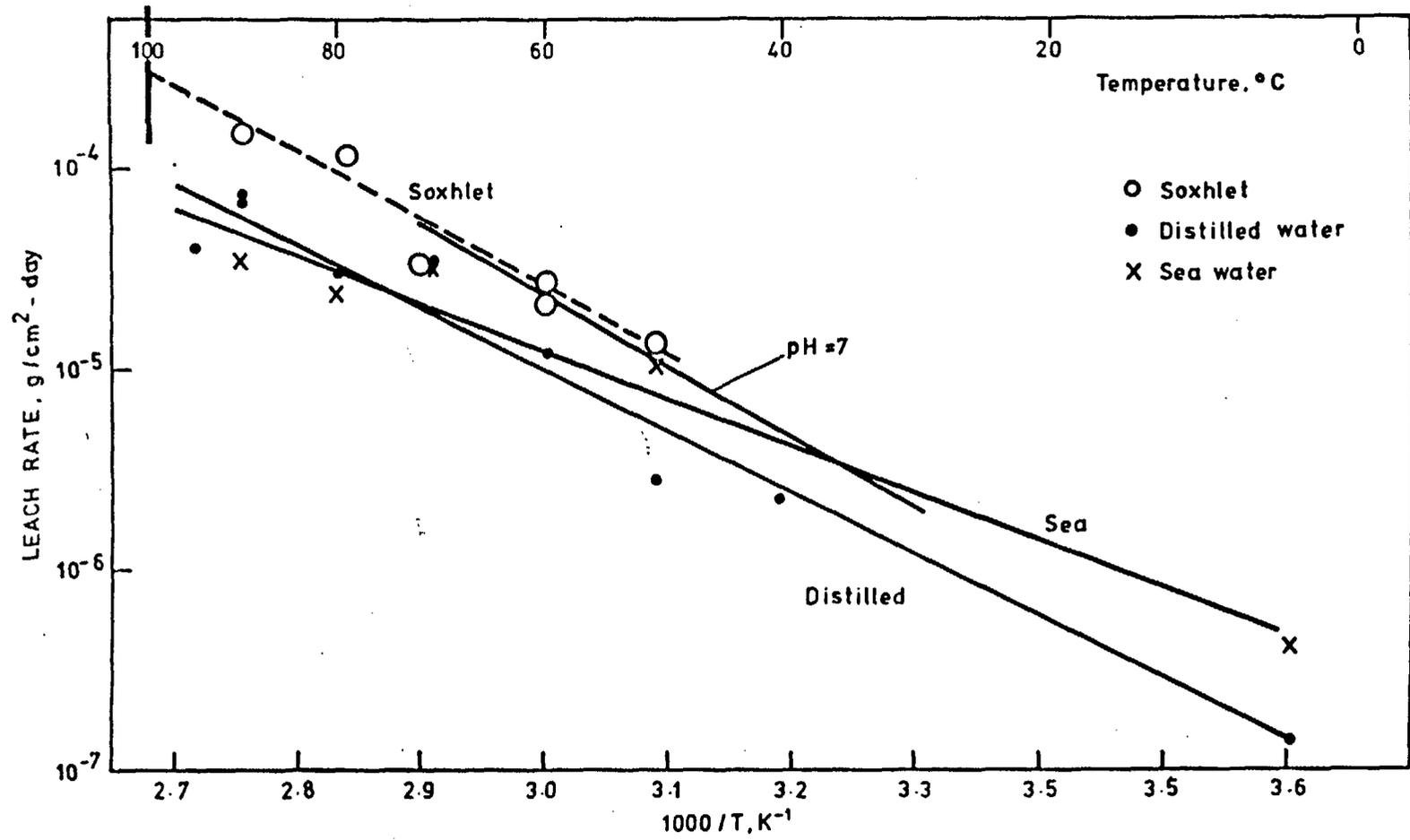


Figure 2.10 Soxhlet and static water leach rates for glass 209. The vertical line at 100°C shows the spread of 11 different Soxhlet results. (24)

#### 2.3.4 Temperature and Hydrothermal Effects

The quantity of alkali extracted from a glass in a given period of time increases with increasing temperature. The type of reactions which control the release of radioisotopes in waste glass are also affected by temperature. For most silicate glasses, the quantity leached in a given time is nearly doubled for every 8°C to 15°C rise in temperature and the reaction rate increases by a factor of 10-100 for every 100°C increase in temperature, depending on the composition of the glass and the type of alkali ion. Some workers<sup>(9)</sup> have attempted to express the temperature dependence of alkali extraction in terms of the Arrhenius equation. However, it is not easy to assign a single activation energy, since alkali extraction is always associated with pH changes and these depend not only on the quantity of alkali released but also on that of silica. Further, below approximately 80°C, a siliceous layer forms on a glass which acts to retard further leaching. Metasomatic reactions, in which new crystalline compounds form from some of the glass constituents, can also occur at the glass surface, particularly at elevated temperatures. Such complications make it difficult to theoretically define a single rate-determining step in a given temperature range. Nevertheless, for a large number of nuclear waste glasses, the apparent leach rate follows the single activation energy Arrhenius equation.<sup>(30)</sup> For PNL waste glass,<sup>(29)</sup> such an observation was made as shown in Figure 2.11; representative leach rates at 25°C are  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$  g of glass/cm<sup>2</sup>-day. Representative leach rates at 40-50°C are  $5 \times 10^{-6}$  to  $5 \times 10^{-5}$  g of glass/cm<sup>2</sup>-day. Similar results for U.K. waste glass 189 and 209 were reported by measuring the leach rate over a range of temperatures using static and Soxhlet methods. The results are shown in Arrhenius plots in Figures 2.9 and 2.10.<sup>(24)</sup> White<sup>(30)</sup> has found the expected exponential increase in rate with temperature well up to the hydrothermal range. This is noteworthy for the assessment of waste glass durability since accelerated testing at high temperature may be a valid means for the simulation of leaching over geological time as a result of this single activation process. However, it is premature to define the leaching mechanism based on these activation analyses due to a lack of data and the system's complexity, which is described below.

In hydrothermal environments, the complexity is more significant since glass is altered rapidly if the temperature is sufficiently high. Although it is generally assumed that the maximum temperatures at which water will contact a solidified waste form in a repository are more likely to be in the range of 150°C, or less, substantial research efforts have been invested in hydrothermal reactions of waste glass in the last two years.

Hydrothermal effects were investigated at Sandia on a copper borosilicate glass (PNL 76-199) with simulated Barnwell fission product oxide waste.<sup>(31)</sup> The tests were conducted in autoclaves for periods of 1 week to 3 months at 250°C and 16.5 MPa. The leach solutions used were: (1) deionized water; (2) high Mg<sup>+2</sup> (35,000 ppm) saturated brine; (3) saturated NaCl brine with low Mg<sup>+2</sup> (10 ppm); and (4) seawater. The rate of corrosion and cesium extraction increased in the order: deionized water < NaCl brine < MgCl<sub>2</sub> brine < seawater; lower pH values lead to higher cation solubilities. Gel layer cracking was reported in glass exposed to deionized water. Devitrification was evident but no crystalline phases were identified.

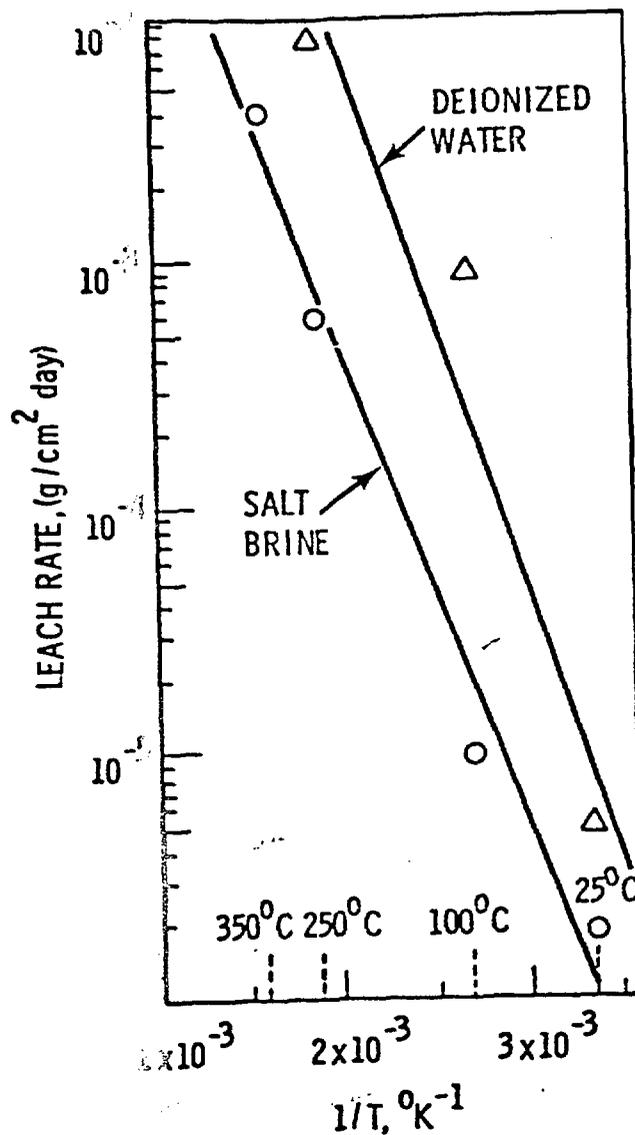


Figure 2.11 Leach rate of waste glass as a function of temperature. (29)

Tests conducted on PNL 76-68 glass at 300°C and 300 bars in deionized and artificial Hanford groundwater, resulted in the conversion of the glass sherds to crystalline and non-crystalline products plus dissolved species in a two week period. The major products were  $(Cs, Na, Rb)_2(UO_2)_2(Si_2O_5) \cdot 4H_2O$  (weeksite) and pyroxene-like phases  $(Na, Ca)(Fe, Zn, Ti)Si_2O_6$  (acmite, augites). High  $Na_2O$  and low  $SiO_2$  may be responsible for the rapid alteration of the sample. The PNL results indicate that the alteration of the glass pellet was higher in deionized water than in brine by a factor of 10 (see Tables 2.2-2.4)

Table 2.2

Percent Element in Solution After Hydrothermal Treatment of 76-68 Glass<sup>(32)</sup>  
(4 Weeks at 300°C and 300 Bars)

	Cs	Sr	La	Nd	U	Zr	Na	Rb	Ca	Ba	Zn	Si	Mo	B	Fe	Ni	Cr
Deionized water	5.0	0.2	0.5	--	0.03	---	45	8.7	1.2	0.1	0.05	4.6	72	93	0.02	4.0	27
USGS NBT-6a brine	52	49	26	11	18	0.05	--	53	---	---	33	---	3	48	0.02	10.4	1.1

Table 2.3

Leachability Results of 76-68 Glass and  
Super-Calcline SPC-4 at 350°C<sup>(32)</sup>

Test	Material	Solution	Time	Leach Rate Based on Weight Loss (g/cm <sup>2</sup> -d) <sup>a</sup>	Percent of Element in Solution <sup>b</sup>							
					Cs	Rb	Sr	Mo	Si	B	U	Zn
1	Glass 76-68	Brine	7 d	$4.0 \times 10^{-3}$	66	72	3.6	54	0.2	71	<0.1	0.5
2	Glass 76-68	Brine	7 d	$4.6 \times 10^{-3}$	80	82	3.4	59	0.2	73	<0.1	0.3
3	Glass 76-68	Brine	21 d	$4.5 \times 10^{-3}$	95	90	4.8	62	0.1	89	<0.1	0.3
4	Glass 76-68	Brine	21 d	c	70	96	3.4	c	0.1	89	0.2	0.6
5	Glass 76-68	Deionized Water	7 d	$5.3 \times 10^{-3}$	6	16	0.2	49	2.2	100	0.1	<0.1
6	Glass 76-68	Deionized Water	21 d	$4.0 \times 10^{-3}$	4	20	0.4	63	1.9	86	0.2	<0.1
A	Super- calcline SPC-4	Brine	30 d	c	46	80	3.3	0.6	0.5	c	c	c

<sup>a</sup>Weight loss of a cylinder of material divided by its geometric surface area and time.

<sup>b</sup>Each test included roughly 20% by weight of a solid cylinder and 80%-325 mesh powder. The majority of ions in solution were leached from the powder.

<sup>c</sup>Not available or not present.

Table 2.4  
Results of Scouting Autoclave Leach Tests  
of Various Glasses, Ceramics and Minerals at 250°C (32)

Sample Material	Leach Rate, g/cm <sup>2</sup> -day <sup>a</sup>		
	50 mL Brine Solution	150 mL Brine Solution	50 mL Deionized Water
Soda-lime-silica glass (NBS No. 710)	3 x 10 <sup>-3</sup>		
Borosilicate glass (NBS No. 717)	5 x 10 <sup>-4</sup>		
Waste glass 72-68	7 x 10 <sup>-4</sup>		
Waste glass 76-68	2 x 10 <sup>-4</sup>	2 x 10 <sup>-3</sup>	8 x 10 <sup>-3</sup>
Granite	6 x 10 <sup>-4</sup>		
UO <sub>2</sub> fuel pellet	2 x 10 <sup>-4</sup>		
Alumina	2 x 10 <sup>-4</sup>		
Sintered Supercalcine (SPC-2)		4 x 10 <sup>-4</sup>	

<sup>a</sup>Samples immersed in simulated WIPP "B" brine for 72 hr at 250°C and 1000 psi. Leach rate based upon weight loss and geometric surface area.

As a result of these tests the role of water under hydrothermal conditions may be described as follows:

- (a) Crystallization catalyst: acts to convert a Na-Fe rich glass into Na-Fe rich crystalline pyroxene-like phases
- (b) Solvent and transport medium: dissolves and transports Cs, Na, U, and Si from a glass at weeksite-like crystalline
- (c) Reactant: forming hydrated weeksite-like phase and a hydroxyapatite.

Additional research reported hydrothermal alteration of powdered sodium zinc borosilicate glass at temperatures up to 200°C.<sup>(33)</sup> Zincsilite is a major product in the alteration. The addition of ZnO was found to improve durability at 100°C through the formation of a Zn-rich alteration zone. ZnO is said to promote subliquidus immiscibility in borosilicate glasses.

Under hydrothermal conditions, alteration is a major variable influencing the enhanced leach rate. Since the alteration is accompanied by complications such as stress generation, a delineation of the mechanisms involved in hydrothermal leaching is not easily achieved.

### 2.3.5 Reprecipitation

The dissolved silica begins to recrystallize under prolonged leach conditions. Barkatt<sup>(34)</sup> observed the recrystallization of Pyrex glass in water at a pH of 9.5. It was further observed that multivalent ions and species are tightly bound to the matrix by the recrystallization process. Recrystallization has received recent attention as a result of its effect on the measurement of leach rates by solutions analysis. It is quite easy to distort leach data by ignoring the analysis of precipitates in solution. When, under what conditions, and to what extent precipitation takes place depends largely on the system. The controlling mechanisms and accompanying variables are only recent subjects requiring further investigation.

## 2.4 Effects of Various Glass Characteristics

### 2.4.1 Glass Composition

Before presenting specific illustrations of compositional effects on the chemical durability of commercial and waste borosilicate glass, we will briefly outline a general approach taken by Adams, et al.<sup>(35)</sup> to "force-frit" complex commercial glasses into a ternary description composed of network formers,  $B_2O_3$ , and network modifiers. The sum of network formers is described as  $XO_2$  which replaces  $SiO_2$  in the ternary scheme and generally consists of additional oxides such as  $Al_2O_3$ ,  $ZrO_2$ ,  $TiO_2$ ,  $Fe_2O_3$ ,  $Cr_2O_3$ ,  $P_2O_5$ ,  $Y_2O_3$ ,  $MoO_3$ ,  $TeO_2$ ,  $La_2O_3$ ,  $CeO_2$ ,  $Pr_6O_{11}$ ,  $Nb_2O_5$ ,  $Gd_2O_3$  and  $Sm_2O_3$ . Network formers are known to be relatively insoluble in water. The network modifiers include the sum of all alkali oxides,  $R_2O$ , such as  $Na_2O$ ,  $K_2O$  and  $Li_2O$ . They generally weaken the networks and are readily soluble in water. The alkaline earths or divalent atoms,  $RO$  can be considered as part of  $XO_2$  since they generally enhance water durability, or as part of the  $R_2O$  since the role of  $RO$  in the formation of crystallographic structures is similar to that of  $R_2O$ .  $RO$  includes oxides such as  $CaO$ ,  $MgO$ ,  $PbO$ ,  $ZnO$ ,  $BaO$ ,  $SrO$  and  $NiO$ . In this study compositions of various commercial borosilicate glasses were plotted in the ternary system of  $XO_2 - B_2O_3 - R_2O(+RO)$  (Figure 2.12). Approximations were made for the lines of equivalent durabilities (isodurs) using a model based on the correlation between the integrity of crystallographic structure and the chemical durability. Numbers 1, 2, and 3 are in decreasing order of the chemical durability. Since their model is empirical in nature and supported by experimental data, the contour lines illustrate fairly well the general trend of the composition effect.

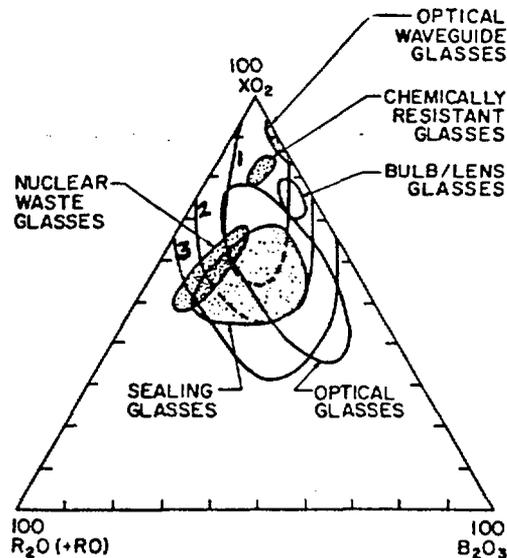


Figure 2.12 Commercial glass composition areas.<sup>(35)</sup>

The composition effect has been studied, qualitatively in most cases, (5,7,9,15,32,33) by considering whether the component: (1) is thermodynamically stable in a given pH-temperature range and affects the thermodynamic stability of other components; (2) affects the formation of insoluble surface film and concomitantly retards or accelerates the surface dissolution rate; (3) affects the diffusion rate of certain ions responsible for the observed dissolution rate (such ions include hydrogen ions, hydronium ions or other cations); (4) influences the solution chemistry, especially the pH; and (5) changes the crystallographic structure of the network leading to a change of dissolution rate. The studies vary from simple binary systems to complex multicomponent systems while the majority restrict their tests to room temperature. Nevertheless, as shown in the beginning of this section, the general trend can still be observed from room temperature to maximum 100°C for the borosilicate glass system. A summary of the effects of particular components is given below.

### Network Formers

- $\text{SiO}_2$ : The stability of vitreous silica has been illustrated for a given pH range at room temperature as shown in Appendix A.1. The solubility or dissolution rate increases rapidly at pH above 9 by the increased ionization of silicic acid. The solubility increases linearly with temperature up to 200°C.
- $\text{Al}_2\text{O}_3$ : The addition of  $\text{Al}_2\text{O}_3$  slightly increases alkaline durability and mechanical abrasion resistance. Presumably this improvement is attributed to: (1) decreased mobility of hydronium and alkali ions, (2) formation of a protective aluminosilicate film in a static condition, (3) the stabilization of calcium-silicate-rich film, and (4) the reduction of the effect of pH in the glass dissolution.
- $\text{ZrO}_2$ : A small amount of  $\text{ZrO}_2$  (about 2 weight percent) increases acid and alkaline durability. The hydrated  $\text{ZrO}_2$  surface is stable at all conceivable pH ranges and offers a very high activation barrier for the diffusion of other ionic species.
- $\text{TiO}_2$ : Similar to  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ,  $\text{TiO}_2$  is expected to increase in chemical durability. However, no measurements of ionic mobilities are available.
- $\text{P}_2\text{O}_5$ : An extensive investigation of corrosion reactions of an inert soda-lime-silica glass containing  $\text{P}_2\text{O}_5$  has been conducted because of the incredible property of the glass to form a strong and stable bond with living bone. This is attributed to the formation of a stable calcium phosphate film when in contact with an aqueous environment (type III surface in Figure 2.1), occasionally accompanied by the formation of a fine-grained polycrystalline apatite mineral phase.

### B<sub>2</sub>O<sub>3</sub>

B<sub>2</sub>O<sub>3</sub> causes a reduction in the diffusion coefficient of alkali ions. In Pyrex borosilicate glass, the diffusion coefficient is low compared to other silicate glasses, including fused silica, and it also accelerates inert film formation as in the case of the P<sub>2</sub>O<sub>5</sub>-containing glass. The extracted B<sub>2</sub>O<sub>3</sub> acts to neutralize the alkali and reduce the solution pH. These effects combine to increase glass durability.

### Network Modifier: R<sub>2</sub>O

As the amount of monovalent alkali element increases with the remaining constituents held in the same ratios, the rate of reaction with water increases. In static solutions this trend is primarily related to the increase in the total quantity of alkali in solution surrounding the glass. This leads to a progressively more alkaline solution and a rapid attack of the glass. The diffusion coefficient of alkali increases as the amount of alkali in the glass increases. This increased reaction rate has also been interpreted in terms of surface effects (type IV surfaces in Figure 2.1).

The relative durability "contribution" of ions among the R<sub>2</sub>O group is in the order is Li<sub>2</sub>O > Na<sub>2</sub>O > K<sub>2</sub>O. Their role in the formation of a durable SiO<sub>2</sub>-film is reflected in this order. It has been observed that the hydronium ions have a higher mobility in potassium. Also, from the thermodynamic point of view, the absolute stability increases in the above order.

If a second alkali oxide, such as potassium, is added to a sodium glass, the durability of the glass is reported to increase. The increase is greatest when the molar ratio of alkali ions is about equal. This increase is a result of the "mixed-alkali" effect, in which the mobility of an alkali ion is reduced when another alkali ion is added, or when the second alkali aids film formation leading to a limited surface attack.

### Network Modifier: R<sub>0</sub>

- CaO: The addition of calcium oxide improves the durability and reduces the extent of selective alkali leaching (up to approximately pH 10). It appears that the addition of calcium lowers the mobility of alkali and hydronium ions. When the alkali ions are lost during corrosion, they leave behind a much more stable CaO-SiO<sub>2</sub> rich film reducing the surface dissolution rate. However at high temperatures, CaO greatly weakens the glass network.
- MgO, SrO, BaO, CdO: These oxides of divalent metals give a similar enhancement of durability as CaO. SrO is known to provide a greater resistance to the destruction of the above-mentioned calcia-silicate surface film. The addition of BaO is reported to reduce the extent of selective alkali leaching.
- ZnO: ZnO addition to a silicate glass increases its chemical durability in the alkaline range up to approximately pH 13, and is

susceptible to vigorous alkaline attack above pH 13. Also, zinc-containing glass will be susceptible to acid attack up to approximately pH 5.5.

- PbO: It is generally known that lead oxide increases the alkaline durability and decreases the acidic durability.

The preceding discussion on the composition effects and the particular mechanisms involved was aimed at providing a brief summary on a complex subject. Most of the data presented were obtained for relatively simple systems (usually ternary components). As the number of components increase, the characteristics described should be modified to some extent, especially when nuclear waste is incorporated. Quantitative measurements relating to composition effects are scarce at the present time. One attempt made by PNL<sup>(37)</sup> centered on the effects of 26 oxides in a generic study of defense waste glass. Chemical durability was tested in acid and basic solutions, at RT and 99°C, in distilled water; percent weight loss was determined for each of the samples. Table 2.5 is a summary of the results which shows a general agreement with the summary of each component described previously. In addition, the effects of U<sub>3</sub>O<sub>8</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and NiO were observed. These types of studies are useful in determining the effect that a certain component may have in a specific glass composition.

Table 2.5  
Summary of Defense Waste Glass Durability<sup>(37)</sup>

Oxide Components	Base Glass, wt%	Variation, wt%	Durability		
			99°C Distilled Water	pH-4	pH-9
Li <sub>2</sub> O	3.0	0-6.0	++	++	0
Na <sub>2</sub> O	13.9	5.0-15.0	++	++	0
K <sub>2</sub> O	0	0-6.0	++	++	0
MgO	0	0-3.0	+	++	0
CaO	4.53	0-6.0	0	++	0
BaO	0	0-3.0	++	++	0
U <sub>3</sub> O <sub>8</sub>	1.53	0-4.0	-	0	0
TiO <sub>2</sub>	7.5	0-10.0	-	--	0
MnO <sub>2</sub>	2.58	1.16-4.0	-	+	0
Fe <sub>2</sub> O <sub>3</sub>	7.9	0.39-15.41	0	+	0
NiO	0.53	0-3.0	0	0	0
ZnO	0	0-7.0	++	++	0
B <sub>2</sub> O <sub>3</sub>	7.50	5.0-15.0	0	++	0
Al <sub>2</sub> O <sub>3</sub>	11.60	1.56-21.64	-	++	0
SiO <sub>2</sub>	39.4	---			0

0 indicates negligible change with increase in this component, + and - indicate increases or decreases, and ++ and -- indicate large increases and decreases with component increase.

A PNL study (38,39) on the generic effects of composition on waste glass properties was conducted where testing involved a systematic variation of glass components. The fitted models used in the prediction of glass properties are shown below. Figure 2.13 gives the predicted Soxhlet weight loss of a four component mixture including the defense waste calcine. The general trend is consistent with our previous summary with the exception of complications arising from the addition of  $B_2O_3$ . However, as the number of glass components increases, complications are compounded due to interactions among the various components as shown in the test of the 11 components (Figure 2.14).

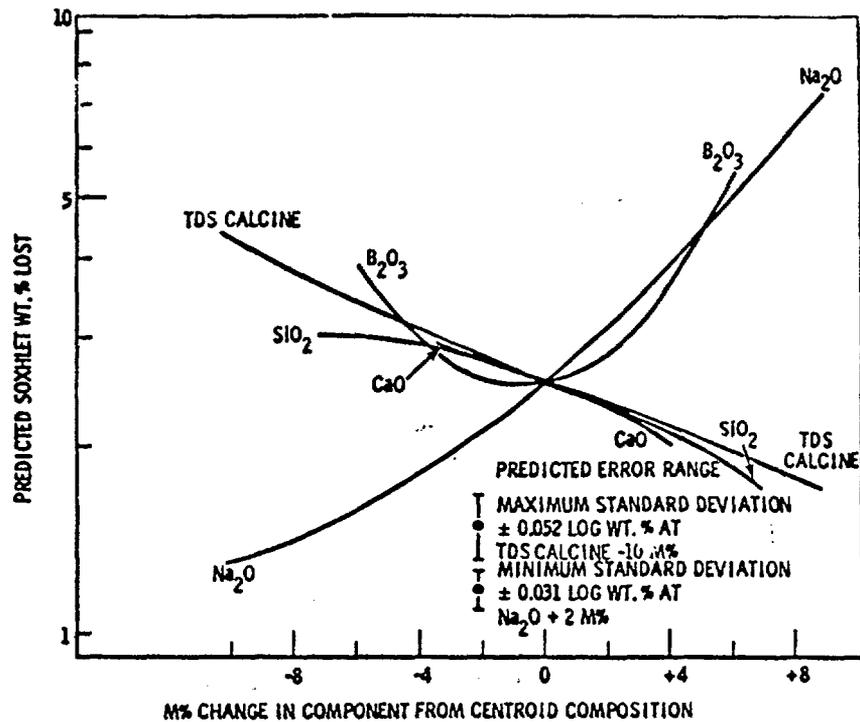


Figure 2.13 Effects of components of PNL four components glass on Soxhlet leach rate. (38,39)

This type of graphical presentation of compositional effects is useful in illustrating multicomponent effects such as in nuclear waste glass although experimental data are very limited at the present time.

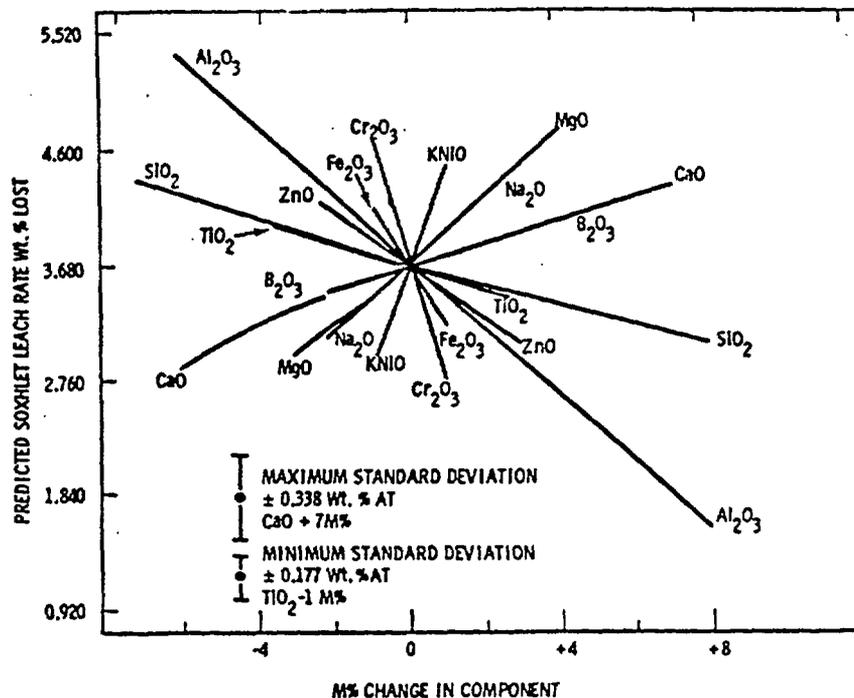


Figure 2.14 Soxhlet leach rate vs change in component from centroid of PNL 11 components glass<sup>(38,39)</sup>

#### 2.4.2 Phase Separation

The chemical durability of phase-separated glasses is closely related to the microstructure. The microstructure of phase-separated glasses may be classified into three types, namely (a) an interconnected microstructure; (b) chemically more durable (e.g., SiO<sub>2</sub> rich) phase particles dispersed in the chemically less durable (e.g., Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> rich) phase matrix; and (c) chemically less durable phase particles dispersed in the chemically more durable phase matrix. The chemical durability of glass deteriorates with phase separation when the glass exhibits microstructural types (a) and (b); chemical durability remains increased or relatively unchanged when the glass durability was found to depend primarily upon the composition of the chemically less durable phase.

The presence of phase separation in borosilicate glasses strongly influences their chemical durability. There is evidence that commercial Pyrex borosilicate glass separates into a disconnected sodium borosilicate phase in a silica-rich matrix, on a scale of 20Å or less, contributing to chemical durability. However, as Pyrex borosilicate is heated to 600°C or higher, its durability deteriorates as a continuous sodium borosilicate phase separates from a silica-rich phase. Previous studies by Skatulla et al.<sup>(40)</sup> for Pyrex-type glass have illustrated the phenomenon of decreased durability due to phase separation. Transitions in behavior between a discontinuous to a continuous microstructure also depend on the types of glass considered. For most commercial borosilicate glasses, the phase separated microstructure results in a reactivity of the glass akin to that of a high silica phase lead-

ing to high chemical durability. Sometimes even when the sodium borosilicate phase was continuous it could not be easily etched out because of the high pressure needed to force liquid water through capillaries 30 Å in diameter. However, as the interconnected microstructure becomes bigger, the soluble sodium borosilicate phase will be easily etched out.

The immiscibility boundaries of the system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  have received the widest attention since this system is the basis of many commercial borosilicate glasses. An illustration by Haller, et al.<sup>(41)</sup> is reproduced in Figure 2.15 where three boundary regions are observed at various temperature ranges. A variety of sodium borosilicate glasses containing up to about 10%  $\text{Na}_2\text{O}$  and from about 10% to 70%  $\text{B}_2\text{O}_3$  (balance:  $\text{SiO}_2$ ), can readily separate into two phases; other elements such as calcium oxide and aluminum oxide reduce the tendency to phase separation. Currently, several places in the U.S. are involved in research on the immiscibility gap for nuclear waste borosilicate glass.

The surface of commercial glasses will sometimes exhibit a slightly different composition from that of the bulk. This compositional difference can be accentuated through phase separation, resulting in a considerable difference in the chemical durability of the surface layer. One example<sup>(42)</sup> is commercial borosilicate glass with an interconnected microstructure having an excess  $\text{Al}_2\text{O}_3$  concentration in the surface layer. Excess  $\text{Al}_2\text{O}_3$  lowers the HF etch rate because of the lower extent of phase separation on surface.

Researchers have considered the possibility of increasing the driving force for crystallization by prior glass phase separation. However, there is no consensus on this point nor any experimental evidence for demonstration.

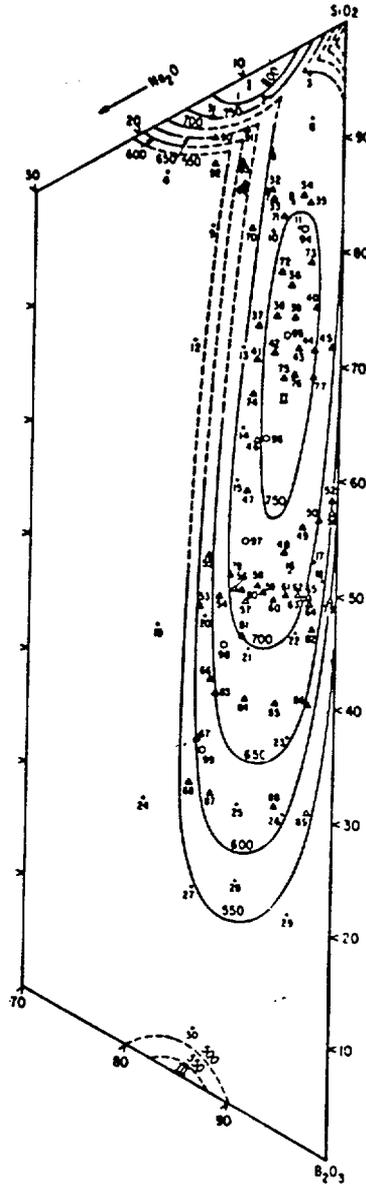


Figure 2.15 Immiscibility boundary of  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  glass system.(41)

### 2.4.3 Devitrification

The effects of devitrification on corrosion are dependent on the composition and the degree of devitrification. In a simple system such as 33L glass,<sup>(19)</sup> 90% crystallization improved corrosion resistance considerably when tested for 120 hrs at 95°C. This is attributed to the absence of a compositional gradient across the phase boundaries between the glass and the crystals. However, in practical systems, the composition of the crystalline phase is different from that of the glass, leading to a measurable attack of the glass phase. In fact, PNL 72-68 which was devitrified at 700°C showed an increase in Soxhlet leach rate of nearly one order of magnitude.<sup>(19)</sup> When the extent of devitrification is reduced, a very small change (less than a factor of 5) in leach rate was observed in 72-68 glass, and no difference was reported in 76-68, 77-107 and 77-260 glasses.<sup>(43)</sup> In nuclear waste repository conditions, the thermal devitrification rate is so low that the enhancement of the leach rate may not be significant: at most an increase of a factor of 10 which is well within the leach rate variations observed between waste glasses of different compositions.

There is a possibility that devitrification affects leach rate indirectly. PNL 76-68 glass in a hydrothermal environment (300°C and 300 bars water) showed that crystalline phases may be responsible for the subsequent glass fragmentation which increases the exposed surface area leading to an enhanced leach rate.<sup>(32)</sup> The formation of a zinc-rich alteration zone was reported as being composed of mainly zincsilite under hydrothermal conditions in sodium zinc borosilicate glass.<sup>(33)</sup> This alteration was presumed to be responsible for an improvement in durability. No comprehensive results are available at present on these indirect effects.

### 2.4.4 Glass Surface Area (SA) to Solution Volume (V) Ratio

Several investigations have firmly established that the corrosion rate increases as the SA/V ratio increases for static corrosion conditions. The data also show that increasing SA/V is a valid means of accelerating the rates of the static attack of glass surfaces. One example is given in Appendix A where the alkali extracted from borosilicate and soda-lime powder specimens with the areas of 7000 cm<sup>2</sup> was compared with the weight lost by plate glass specimens of 100 cm<sup>2</sup>. For bulk glass surfaces, the quantity of a specified glass constituent in solution at a given time is directly proportional to the (SA/V) ratio, namely the constants, a and b of Equation 1 include the linear term (SA/V). No systematic data of (SA/V) are available for commercial borosilicate glass. The following is a summary of a recent study on nuclear waste borosilicate glass.

Under static leaching conditions, it was shown that the loss of alkali or alkaline earth species from glass to an aqueous media increases the solution pH and concomitantly leads to a transition from  $t^{1/2}$  kinetics to  $t$  kinetics. The progressive increase in solution pH for PNL 72-68 under static leaching conditions at 120°C and 15 psi in distilled water is shown in Figure 2.16 for various (SA/V) ratios.<sup>(19)</sup> It is shown that the increase of (SA/V)

as a function of (SA/V) ratios for various glasses including 72-68 glass at different temperatures. When the logarithm of the time required for the glass to reach a specified level of attack is plotted, similar features will be obtained. The surface attack becomes greatly accelerated at high (SA/V) ratios and only short times are needed to show surface deterioration. Additional data on nuclear waste glass are currently being generated in several laboratories.

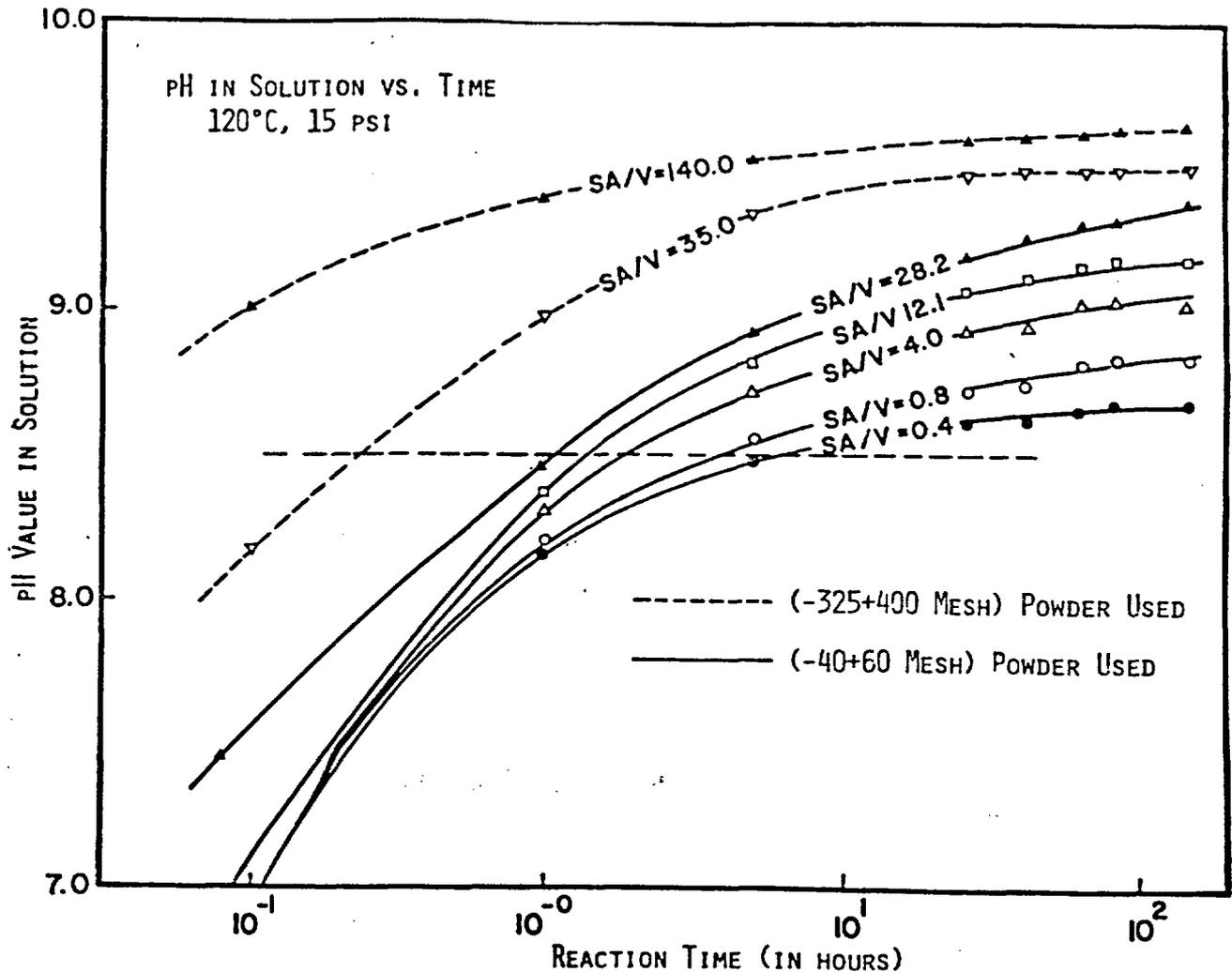


Figure 2.16 Solution pH vs exposure time for various surface area-to-solution volume ratios (SA/V). (19)

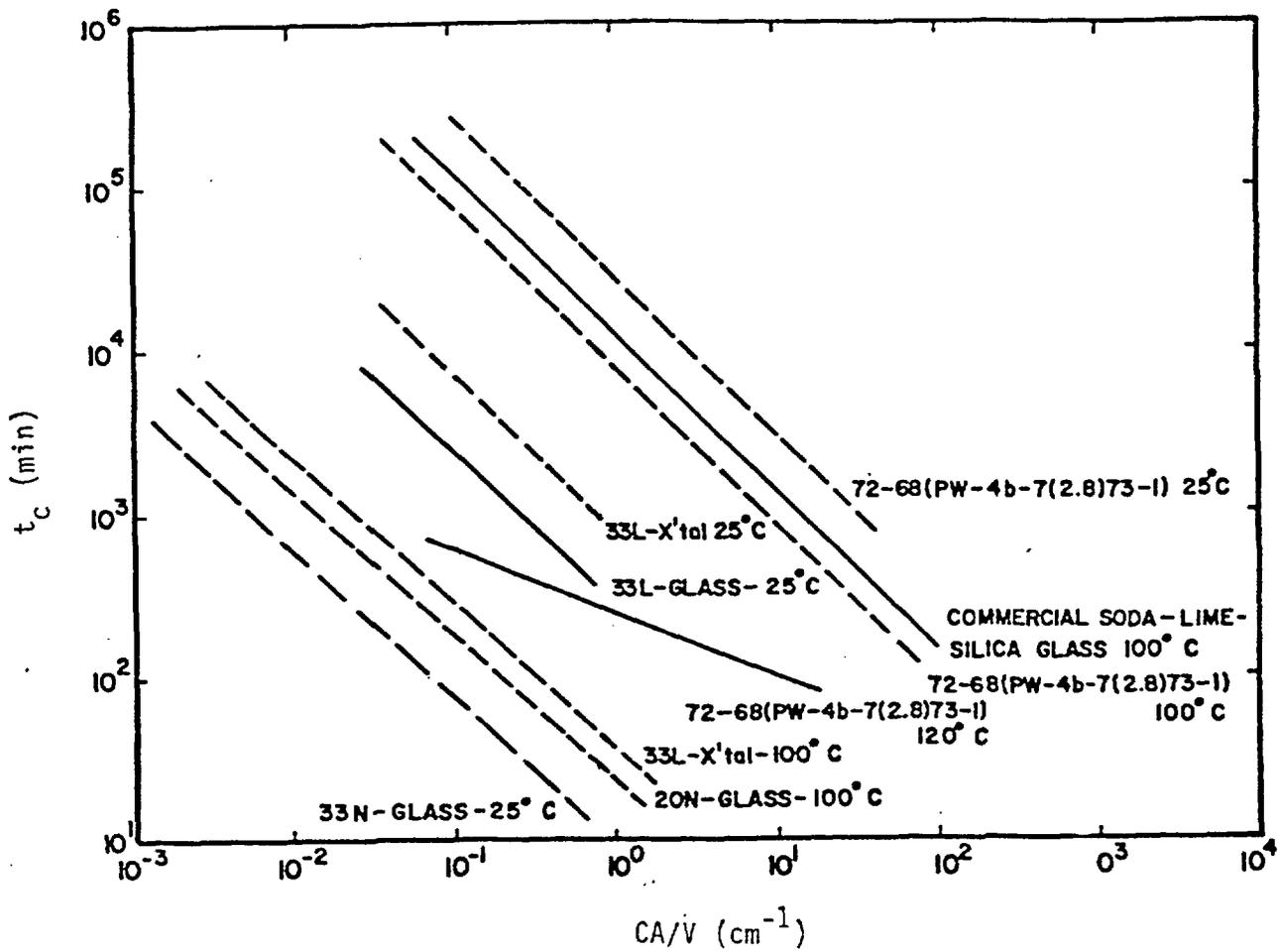


Figure 2.17 Changeover time in kinetics ( $t_c$ ) as a function of (SA/V) for various materials. 72-68 is a zinc-borosilicate simulated nuclear waste glass; 33L-X'tal is the divitrified 33L glass; 33N is a 33 mole%  $\text{Na}_2\text{O}$ -67 mole%  $\text{SiO}_2$  glass; 20N is a 20 mole%  $\text{Na}_2\text{O}$  -80 mole%  $\text{SiO}_2$  glass; and the commercial soda lime glass is a glass container composition. (19)

Tests on powdered glass show complications in the determination of (SA/V) ratios arising from particle geometry, the surface area-time dependence and concentration cells. Particle shapes are complicated, containing sharp edges and even some porosity. The true surface area of these particles decreases with exposure time causing a corresponding decrease in (SA/V). During a static corrosion test, the glass grains settle to the bottom of the container, creating an agglomerate of particles containing concentration cells, and undoubtedly corroding in a manner different from that of the bulk glass surfaces due to local pH variations. Also film formation on smaller particles greatly alters the effective surface area for further reactions and this error becomes more severe the longer the exposure time until the smaller particles are totally dissolved. No quantitative data are now available for the dynamic determination of the effective (SA/V) ratios and its effect on leach rates.

#### 2.4.5 Surface Stress

During the glass leaching process, the surface experiences stresses or swelling arising from hydration, ion exchange or crystallization. They subsequently lead to the spalling or peeling-off of surfaces before the congruent state is reached. For PNL 72-68 and 77-107 glasses leached using the IAEA technique of deionized water at 25°C with weekly changes of leach solution, the glasses exhibited cracked "mud flat" surfaces.<sup>(43)</sup> Surface disintegration was also observed in strontium alumoborosilicate glass by volatile Cs in the temperature range of 550°C-600°C for up to 300 hrs.<sup>(44)</sup> For the above mentioned surface deterioration conditions, the leach rate will rise abruptly due to cracking and partial or complete peeling off of the protective layer. The abrupt leach rate makes it difficult to predict the leaching kinetics of the type described by Equation (1).

Sometimes surface stress generated by the crystallization of the leached layer induces a catastrophic failure of the bulk glass by the propagation of the stress into the interior of the sample. This again will result in an unpredictable leach rate. Glass failure of this type will be discussed further in the section on static fatigue.

#### 2.4.6 Cracking

Considerable controversy exists on the effects of microfracturing in glass leaching. PNL's study of partially devitrified <sup>244</sup>Cm-doped waste borosilicate glass exhibited microfracturing with no accompanying measurable effect on leach rate.<sup>(45,46)</sup> Other groups have, however, considered the significance of cracking.<sup>(15,47)</sup> Recently, a more systematic simulation of cracking was performed by Perez, et al.<sup>(48)</sup> Cracks were simulated by stacking glass pellets with platinum wire spacers and holding them together with a stainless steel clamp. Their findings indicate that crack depth and crack width are important parameters with the possibility of a minimum crack depth limit required prior to enhanced leaching. In some cases, more than a factor of two increase in leach rate has been observed, as shown in Figure 2.18. It should be noted that for most cases, the increased cracked area does not appear to result in a proportional increase in leach rates. The importance of this work lies in its attempt to quantify the effects of cracks on the leach rate of glass. Further work is needed that would tie in this approach to the overall aspects of glass leaching.

#### 2.4.7 Other Pretreatments

Surface chemical and structural variations can arise from a number of sources during the manufacture of glass. Variation in batch formulations including, forming procedures and environments, annealing conditions, subsequent hot end treatments, and exposure history, will affect the observed corrosion behavior during testing.

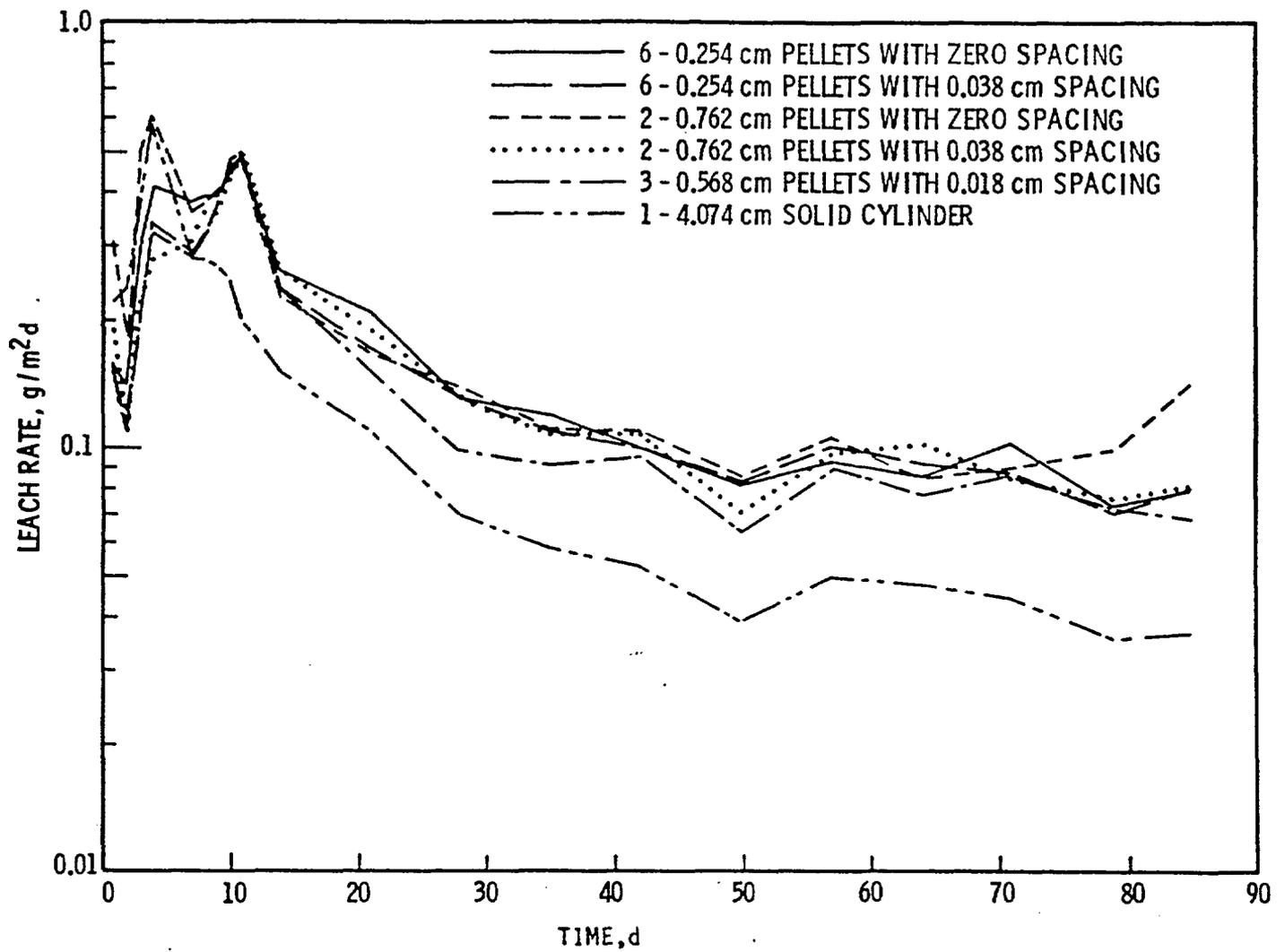


Figure 2.18 Leach rate (g-glass/m<sup>2</sup>-d) based on silicon vs time for 1.90-cm-diameter pellets (solid cylinder is an uncracked sample, and the rest are simulated cracked samples).<sup>(48)</sup>

Generally a more rapid reaction has been observed in the case of quenched glass with water compared to the annealed glass.<sup>(5,49)</sup> This result can be understood from the higher ionic mobility in the quenched glass which has a lower density and a more open structure.<sup>(49,50)</sup> However, the quantity of the enhancement is usually not significant being, at most within a few percent.<sup>(51)</sup> In fact, for the ternary sodium borosilicate glass, no difference was observed between the rapidly quenched glass and the glass annealed for 2 1/2 hours at 600°C.<sup>(35)</sup>

Glass homogeneity also affects leach rates. Inhomogeneity in this case mainly includes the quantity of undissolved constituents. Studies of 76-68 glass with several different thermal histories have shown that the best leach resistance was obtained from the glass exhibiting the best homogeneity.<sup>(19)</sup> A quantitative assessment is not available at present.

Other variables such as surface roughness will also have an effect on leach rates. Sanders, et al. investigated this effect in a binary lithium glass by abrading the surface using various grit sizes.<sup>(52)</sup> Solution analysis showed that the initial rate of silica-rich film formation is most rapid for the smoothest surface. Evidence seems to indicate that surface roughness will also influence static fatigue behavior. Although complex processes are introduced by this parameter, it is clear that the extent of the roughness will have an influence on both the relative and total amounts of material removed from the surface of the glass.

## 2.5 Cation Selectivity and the Diffusion of Ions and Gases

Toxic radioisotopes may escape from the waste form by solid state diffusion. Cation selectivity and the diffusivity of ions and gas molecules are responsible for this process. What follows is a summary of the properties of diffusion and ion selectivity in glass.

Figure 2.19 shows a tabulation of the diffusion coefficient for monovalent sodium ions in various silicate glasses at 386°C.<sup>(6)</sup> Note the range of  $10^{-10}$  cm<sup>2</sup>/sec for Pyrex borosilicate glass, which gives a diffusion distance of approximately 1-2 cm for 1000 years. The distance, however, will decrease by orders of magnitude at temperatures below 100°C. Anions and cations of higher valence diffuse much more slowly than monovalent cations in glass. The self-diffusion coefficients of cations other than alkali ions measured at relatively low temperatures are summarized in Figure 2.20.<sup>(53)</sup> Unfortunately no data are available for borosilicate base glass, where the diffusivity changes by the relative amount of sodium borate phase and the continuous silica phase. As more sodium borate is added to the glass, the absolute value of the diffusivity decreases by the decrease of the effective area of the continuous silica phase. The quantitative amount of this change is not known. For the glassy materials suitable for the long-term storage of highly radioactive wastes, Ralkova<sup>(54)</sup> studied the diffusivity of <sup>137</sup>Cs and <sup>90</sup>Sr in alkali-lime-silicate glass and basalt. In the temperature range of 300°C-600°C, diffusivities were of the order of  $10^{-13}$ - $10^{-11}$  cm<sup>2</sup>/sec in the basalt. Again data are not available for borosilicate base glasses.

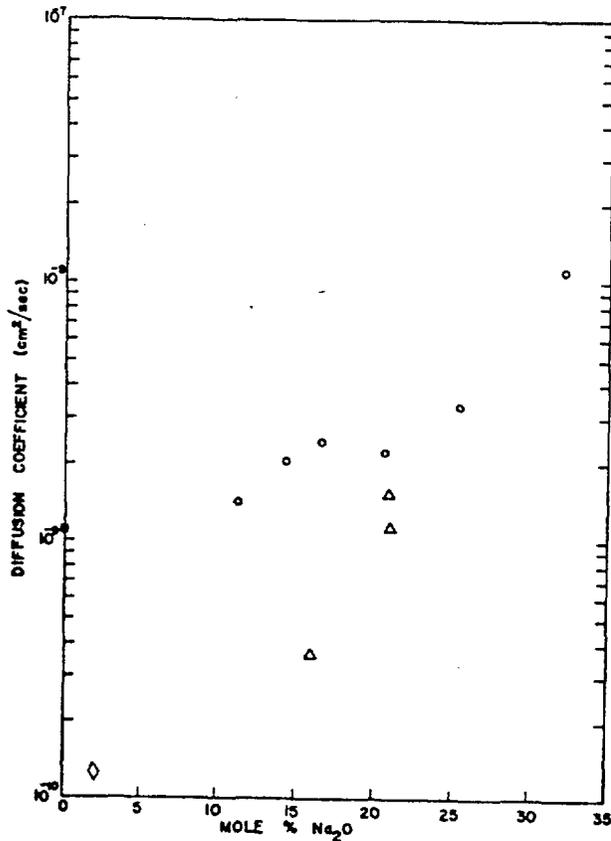


Figure 2.19 Diffusion coefficients of sodium in sodium silicate glasses at 386°C as a function of sodium concentration. ○, binary sodium silicates; Δ, sodium calcium silicates; □, fused silica; ◇, Pyrex borosilicate. (6)

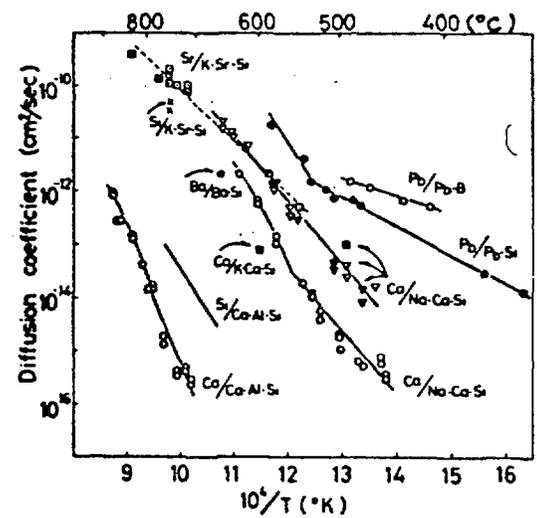


Figure 2.20 Self-diffusion coefficients of  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Pb^{2+}$ , and  $Si^{4+}$  ions in various silicate and borate glasses. (53)

Some diffusion measurements for gases in sodium borosilicate glasses are summarized in Table 2.6. Gas diffusivities are in general higher than the cation diffusivities.

Table 2.6

Molecular Diffusion in Sodium Borosilicate Glass(55-57)

Glass	Gas	Diffusion Coeff. at 200°C
Pyrex	He	$4.7 \times 10^{-7}$
"	D <sub>2</sub>	$4.1 \times 10^{-9}$
Borosilicate*	He	$5.0 \times 10^{-8}$
"	Ne	$7.0 \times 10^{-11}$

(\*60% SiO<sub>2</sub>, 30.5% B<sub>2</sub>O<sub>3</sub>, 9.5% Na<sub>2</sub>O)

The problem of relating glass composition to ion exchange has been studied extensively by Eisenman and co-workers.<sup>(58)</sup> The competing interactions of cations in dilute aqueous solutions are categorized as 11 sequences in a cation selectivity order. Table 2.7 shows the selectivity sequences, related in a definite way to the composition of the glass, which determines the field strength in the table. Data for silicate glasses without boron and aluminum fall to the lower end of the table, whereas the opposite is true for the borosilicates.

Table 2.7

Eisenman's Selectivity Orders Among the Alkali Ions(58)

I	Cs > Rb > K > Na > Li	
I	Cs > Rb > K > Na > Li	
IIa	Cs > K > Rb > Na > Li	or II Rb > Cs > K > Na > Li <sup>a</sup>
IIIa	K > Cs > Rb > Na > Li	or III Rb > K > Cs > Na > Li <sup>a</sup>
IV	K > Rb > Cs > Na > Li	
V	K > Rb > Na > Cs > Li	
VI	K > Na > Rb > Cs > Li	
VII	Na > K > Rb > Li > Cs	
IX	Na > K > Li > Rb > Cs	
X	Na > Li > K > Rb > Cs	
XI	Li > Na > K > Rb > Cs	

<sup>a</sup>Calculated for closely spaced sites.

This basis will not be valid for glasses exhibiting phase separation, hydration, and before electrochemical properties are stabilized. The stabilization in certain cases may take long periods of time.

## 2.6 Weathering

Even though a water solution may be absent, chemical reaction can occur in the presence of water vapor in the atmosphere. Static and cyclic humidity must be taken into account when assessing glass durability. Corrosion will proceed if: (1) the products of ion exchange (notably alkali) remain on the surface; and (2) ambient conditions of relative humidity or temperature are disrupted.

Water adsorption tends to increase with time and humidity; alkali generation increases with time but varies with humidity. Other cations may enhance durability by decreasing the reactivity of the alkali such as Zn, Sr, Ba, Pb, Zr. Zr, for example, reacts to form a tight zirconium alkali-silicate protective layer increasing significantly acid and alkali durability.

Figures 2.21 through 2.25 and Table 2.8 show the results of tests conducted at Corning on the effects of humidity on various glass types.<sup>(59)</sup> The relative humidity (RH) ranged from 30-90%. Weathering effects have been observed down to 30% RH. Certain glasses can weather as much at 30% RH as at 90% RH. Weathering effects have been found to decrease (or slow down) with increasing RH by a dilution effect from adsorbed water.

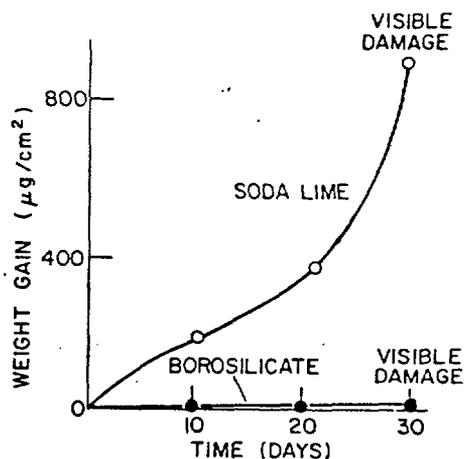


Figure 2.21 Weight change of soda-lime and moderately resistant borosilicate glass after weathering at 89% RH, 50°C.<sup>(50)</sup>

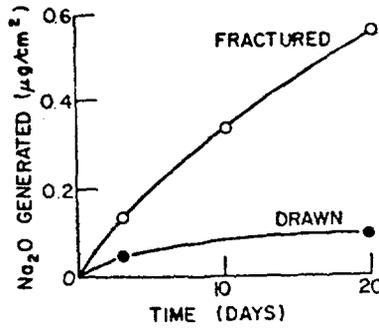


Figure 2.22 Na<sub>2</sub>O on surface after weathering of moderately resistant borosilicate glass tubing at 98% RH, 50°C. (59)

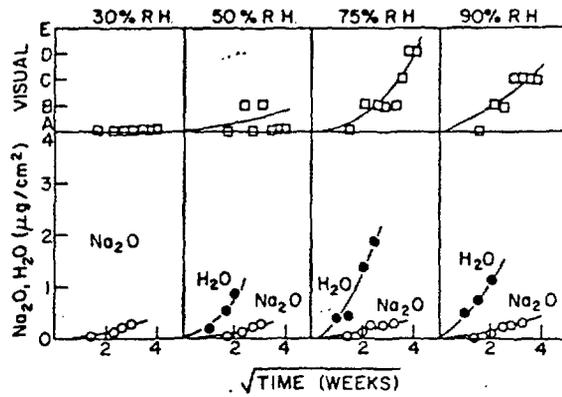


Figure 2.23 Visual appearance, Na<sub>2</sub>O and H<sub>2</sub>O generated on moderately resistant borosilicate glass tubing and power weather at different RH. (59)

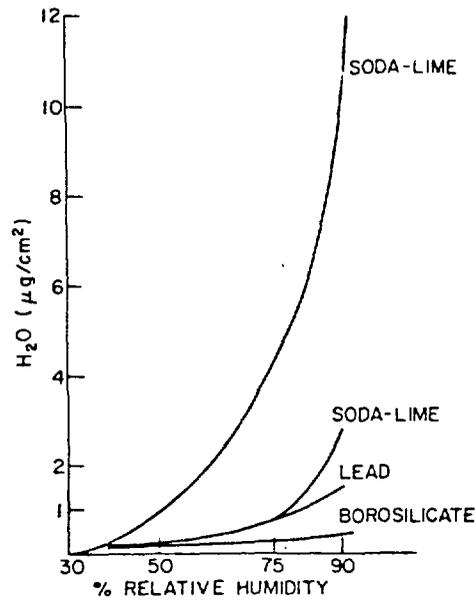


Figure 2.24  $\text{H}_2\text{O}$  adsorbed on several glasses, as a function of RH after 7 days. (59)

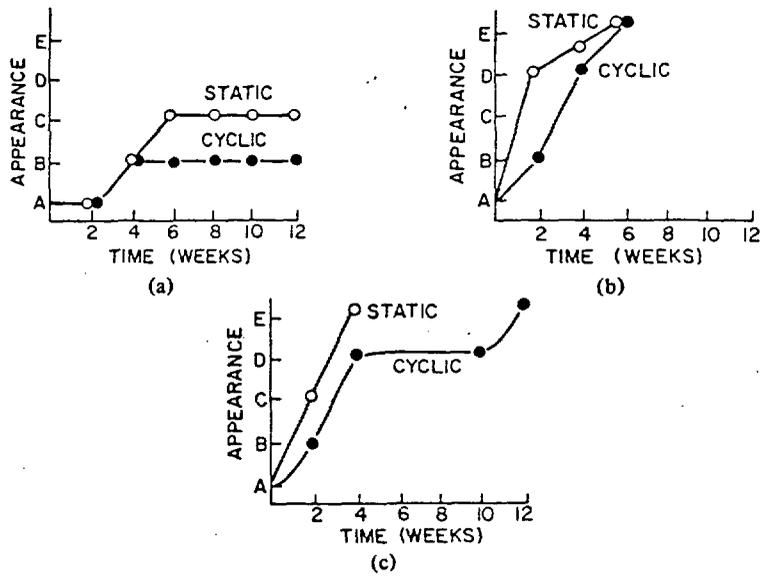


Figure 2.25 The effect of cyclic and static RH on visual appearance. (a) for borosilicate tubing, (b) for plate glass, (c) for soda-lime tubing. (59)

interpreted as indicative of a linear time dependence of glass dissolution. One of the oldest analyzed decomposed glass is a glass bead dating to approximately 1600 BC.<sup>(68)</sup> The weathering product was found to be impure hydrated silica. Results obtained by Geilmann<sup>(69)</sup> on medieval glasses confirm findings that alkalies and alkali earths are almost completely removed. Aluminum, iron, titanium, and several minor components remain or increase (reprecipitate) in concentration due to exchange or adsorption on the hydrated silica from soil or mineralized groundwater.

The complexity of the weathering process under burial conditions is evident through the examination of ancient glass. Investigations by Brill and Hood at Corning on weathering layers, suggested a periodic or cyclical accumulation of weathered crusts. The initial work involved the examination of ancient soda-lime-silica and potash-lime-silica compositions. Weathering layers (0.3-15  $\mu\text{m}$  thick) tended to correspond to the approximate number of years that the object had been exposed to weathering. Initially seasonal variations (temperature, humidity or wet/dry periods) were suggested as the probable cause for such correlations. However, samples of ancient glass which had been submerged at sea also showed this pattern.<sup>(70)</sup> The layers seen in Figure 2.26 consist of almost pure amorphous silica. Similar results were obtained on borosilicate glasses involved with the production of Vycor-type glass at Corning.<sup>(71)</sup> The correlation between the number of layers and the number of years of exposure has not been given an adequate explanation, although attempts have been made.<sup>(72,73,74)</sup>

These studies also point out the nonuniformity of attack at the glass surface. Figure 2.27 shows a weathering 'plug' occurring beneath the amorphous weathering layers, possibly due to a high concentration of moisture at that point. The semi-circular areas at the top are also indicative of non-uniform weathering at the surface.<sup>(72)</sup> Decomposition begins at a large number of sites on the surface and proceeds into the bulk forming a series of alkali-depleted spherical layered shells which, at some point, will tend to coalesce parallel to the original surface.

The above review presents some evidence on the long-term integrity of various glasses. For a more quantitative study, a data base including profiling, devitrification, and weathering conditions is needed.

Regarding the compositional effect on weathering of glass over geological time periods, analyses of 12th to 16th century glass showed that the most durable samples fell in the compositional range of 70-75% "SiO<sub>2</sub>, low "R<sub>0</sub>" (10-40%) and notably low MgO (1.2-3.2%).<sup>(65)</sup> Conclusions based on the study of medieval glasses indicate that they do not weather noticeably during the 500-800 years of exposure provided the "SiO<sub>2</sub>" content is greater than 60 mole percent. This seems to have been confirmed in additional studies by El-Shamy on K<sub>2</sub>O-CaO-MgO-SiO<sub>2</sub> glasses.<sup>(66)</sup>

X-ray fluorescence analysis coupled with SEM on medieval soda-lime glass and Roman soda-lime glass offer potentially useful insights for comparison into oxide depletion. The results of a profile study on the elemental composition of these glasses is presented in Table 2.9.<sup>(67)</sup> The surface alteration of these glasses was due to weathering processes as a result of near-surface burial.

Table 2.9  
Profiles of Medieval and Roman Glasses<sup>(67)</sup>

Oxide (Weight Percent)	Medieval Glass-YMG 1			Roman Glass-YMG 396		
	Surface: A	B	C	Surface: A	B	C
Na <sub>2</sub> O	3.4	10.9	16.8	n.d.	11.4	18.9
MgO	0.9	0.8	0.8	1.0	0.4	0.4
Al <sub>2</sub> O <sub>3</sub>	1.8	1.7	1.6	6.9	2.4	1.5
SiO <sub>2</sub>	65.9	63.7	68.7	63.8	60.4	70.2
P <sub>2</sub> O <sub>5</sub>	0.8	0.7	0.9	0.4	0.2	0.3
K <sub>2</sub> O	2.0	1.9	1.7	2.0	1.1	1.2
CaO	9.3	9.4	7.2	6.1	7.3	6.0
MnO	0.9	0.9	0.6	1.0	1.1	0.8
Fe <sub>2</sub> O <sub>3</sub>	1.1	1.0	0.9	0.7	0.7	0.6
CuO	0.4	0.4	0.2	0.1	0.1	0.01
ZnO	0.05	0.05	0.03	0.04	0.04	0.03
PbO	0.8	0.8	0.6	0.2	0.2	0.1

n.d. = Not detected; detection limit reported <0.8 weight percent Na<sub>2</sub>O.

A = Surface of sample - untreated.

B = Subsurface region approximately 200 μm below surface.

C = Approximately 500 μm below weathered surface; bulk composition.

If we assume that surface A represents the original surface with no detachment of weathered layers and that the depletion of Na<sub>2</sub>O and SiO<sub>2</sub> have been uniform, the ratios of weight percent oxide loss to geologic time (approximately 800 yrs and approximately 1700 yrs for the Medieval and Roman glass, respectively) appear relatively close. Both samples were found in the same locality and we may assume that they were exposed to similar weathering conditions. The apparent uniformity in Na<sub>2</sub>O/SiO<sub>2</sub> depletion may be

Table 2.8

Summary of Visible Damage and Generated Alkali on Various Glasses Weathered 14 Days at 98% RH, and 50°C<sup>(56)</sup>

Glass Type	Visible Damage	Alkali Generated ( $\mu\text{g}/\text{cm}^2$ )
Alumino silicate	None	<0.01
Alkali borosilicate A	Barely detectable	0.01 to 0.05
Alkali borosilicate B	Slight	0.05 to 0.25
Alkali lead	Moderate	0.25 to 1.0
Soda lime A	Appreciable	1.0 to 5.0
Soda lime B	Severe	>5.0

Crizzling or spalling is a result of the adverse effects of weathering on glass surfaces. Spalling of the surface hydration layer may result where the alkali-depleted network is too weak to sustain stress. The protective layer will act as a barrier only as long as the high silica network remains intact.<sup>(60)</sup> At the Conasauga test site (Tennessee; shale) PNL 75-25 borosilicate glass, subjected to alternating wet-dry cycles, exhibited a 20  $\mu\text{m}$ -thick layer showing network cracks and nonuniform penetration of corrosion into the underlying unaltered bulk glass.<sup>(61)</sup> Spalling has been noted in a variety of archaeological glass compositions that have been subjected to alternate wet-dry cycles. This phenomenon came to the attention of conservators when glasses previously submerged were placed in dry environments for exhibit resulting in the spalling of the hydrated surface layer.<sup>(62)</sup>

Since long-term weathering effects are quite difficult to duplicate under laboratory conditions for the geologic time periods under consideration in nuclear waste management issues, archaeological samples of weathered glass may provide insights into long-term durability.

Shaw,<sup>(63)</sup> using X-ray diffraction and differential thermal analysis, showed that the weathering crust on approximately 300 year-old buried potassium glass had a relatively high degree of crystallinity. Khy and Nauer<sup>(64)</sup> estimated the time period for the crystallization based on solid state transformation kinetics for the systems  $\text{Na}_2\text{O}-\text{SiO}_2$  and  $\text{Li}_2\text{O}-2\text{SiO}_2$  at 300 K. The  $\text{Na}_2\text{O}-\text{SiO}_2$  system can be taken as resembling the compositional characteristics found in certain ancient glass forms due to a higher  $\text{Na}_2\text{O}$  and lower  $\text{CaO}$  content. Crystallization by homogeneous nucleation is beyond the range of archaeological consideration (approximately  $10^{17}$  years). If the magnitude of acceleration as influenced by hydroxyl groups is taken into account, homogeneous nucleation will result at approximately  $10^{14}$  years. Crystallization from heterogenous nucleation, assuming "worst case" conditions may occur in approximately  $10^3$  years. Since ancient glasses from periods greater than  $10^3$  years have survived a variety of different weathering environments, Khy and Nauer's assessment is not unrealistic and is confirmed by the long durability of ancient glass compositions.

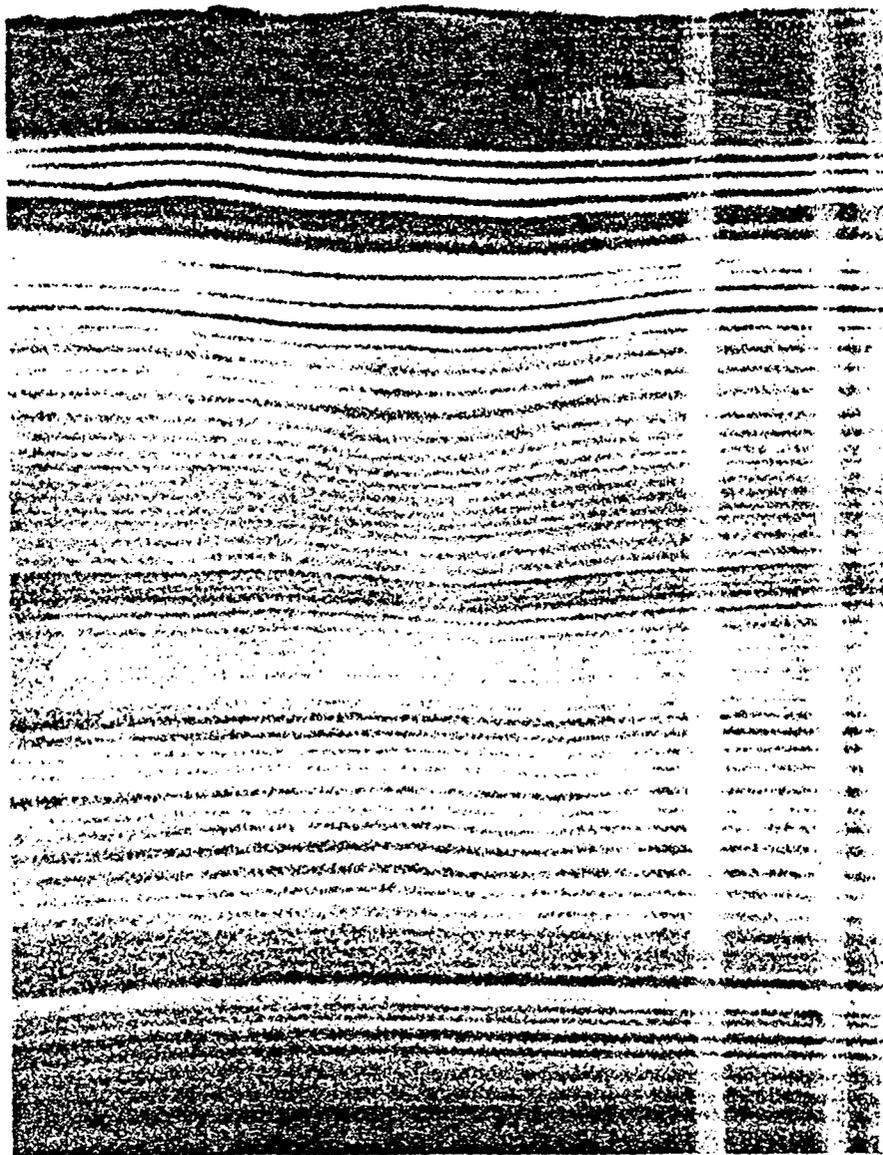


Figure 2.26 Cross section of the weathering crust on a 17th-century wine bottle (x750). Clear substance at top is the supporting plastic. (70)



Figure 2.27 Enlarged (X50) section of a piece of window glass which had been buried for 288 years. The top surface was probably the outside of the window and there are 65 parallel layers at that surface before the 'plug' adds another 220 layers. Far fewer layers occur at this part of the lower surface. (72)

### 3. LOCAL CORROSION AND STATIC FATIGUE

There are insufficient data at the present time to draw any definitive conclusions on the importance of local corrosion in glass. The evidence seems to suggest that under laboratory conditions local corrosion, such as pitting, is no more severe than general corrosion.<sup>(51)</sup> Although ancient glass exhibits local attack during weathering processes, experimental data on the effects of this phenomenon with respect to overall durability are not currently available.

Static fatigue, on the other hand, is known to be a very important mode of disintegration for glass in the presence of water. Cracks developed under static fatigue will increase the exposed surface area leading to a significant increase in the leach rate. Due to the importance of this phenomenon, static fatigue mechanisms, time to failure, and pertinent variables such as solution pH, humidity, temperature, pressure, compositions, matrix microstructure and surface flaws, require some discussion.

Static fatigue occurs only in the presence of water which reacts chemically with the strained bonds at the crack tip causing bond rupture. Therefore, static fatigue is a chemical process that involves a stress-enhanced chemical reaction between water and the highly stressed region near the crack tip. The general characteristics of static fatigue are as follows:

- static fatigue occurs generally in the presence of water;
- static fatigue can be detected for load times as short as  $10^{-2}$  second;
- static fatigue is an activated process;
- static fatigue limit is observed in some cases.

#### 3.1 Static Fatigue Mechanisms

Several proposed mechanisms by which the crack extension procedure occurs may be summarized as follows:

- Chemical Corrosion: Highly strained bonds at the crack tip are more susceptible to corrosive agents. The chemical reaction rate theory of Hillig and Charles<sup>(75,76)</sup> and the multibarrier kinetic theory by Brown<sup>(77)</sup> are considered in assuming this mechanism.
- Strain-Gradient Induced Diffusion: This mechanism employs a strain-gradient induced diffusion of mobile ions yielding concentrations of such ions at positions in advance of the crack tip. Enrichment, with respect to these ions at the crack tip, reduces the local Si-O bond strength allowing crack advancement and apparently premature rupture. Gerberich and Stout<sup>(78)</sup>, Cox<sup>(79)</sup>, Hasselman, Stevens and Dutton<sup>(80,81)</sup> proposed slightly different diffusion models.

- o Surface Energy Reduction: Orowan<sup>(82)</sup> attributed static fatigue to an adsorption-induced lowering of the glass surface energy, concomitantly leading to an easier crack growth.
- o Others: A model by Weidman and Holloway,<sup>(83)</sup> proposed that the growth of a plastic zone controls the rate of crack propagation. Fuller and Thomson<sup>(84)</sup> modeled a one-dimensional crack in two semi-infinite chains of atoms. Although these models explain certain features, such as a higher fracture energy than the surface energy, experimental evidence is needed to show that the adjustable parameters or uncertainties in each model can be eliminated.
- o Mechanism Predominance: Depending on the environment, the relative importance of each factor has been determined. For instance, in a corrosive environment chemical corrosion is likely to be the dominant process while the effectiveness of the environment for the reduction of surface energy will be predominant in the presence of noncorrosive environments.

### 3.2 Slow Crack Growth

From fracture mechanics studies, crack velocity  $v$  was found to be a function of a stress intensity factor  $K_I$ . For various glasses of different compositions, Figure 3.1 illustrates the  $K_I$  dependency in water environment.<sup>(83)</sup> Several expressions for this  $K_I$  dependency were developed. In general  $v$  is dependent on  $K_I$  exponentially. The most representative expression is given by

$$v = v_0 \exp[(-E^* + bK_I)/RT] \quad (5)$$

where  $v_0$ ,  $E^*$  and  $b$  are empirical constants representing,  $v_0$ , the initial velocity;  $E^*$ , the activation energy without the applied stress.<sup>(86,87,88)</sup> For borosilicate glass in water

$$E^* = 30.8 \text{ Kcal/mole}$$

$$b = 0.200 \text{ (m}^{5/2}\text{/mole)}$$

$$\ln v_0 = 3.5$$

### 3.3 The Law of Time to Failure

Generally, the time to failure depends on the magnitude and total duration of the load. The time to failure at a given stress level is inversely proportional to the  $n$ th power of the applied stress. The representative equation for the time to failure is given by

$$\ln(t/t_{1/2}) \approx -\beta \sigma_t (\sigma/\sigma_N - 1/2) \quad (6)$$

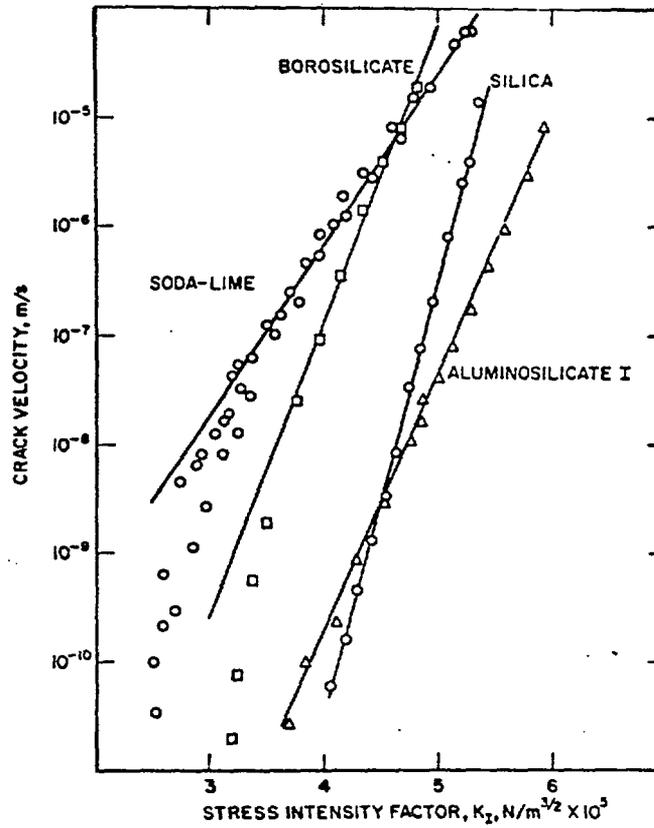


Figure 3.1 Effect of glass composition on crack propagation rate. Tested in water at 25°C. (85)

where  $t_{1/2}$  is the failure time at  $\sigma/\sigma_N = 1/2$ ,  $\sigma t$  is found experimentally,  $t$  is time,  $\sigma$  is applied stress and  $\sigma_N$  is the failure stress at liquid nitrogen temperature. (89) For borosilicate glass with different surface treatments, the following parameters were derived experimentally in a water environment (Table 3.1). (6)

Table 3.1

Parameters for Various Glasses With Different Surface Treatments

Glass	Surface Treatment	Breaking stress at 77°K (kpsi)	$\beta\sigma_t$
FN borosilicate	Abraded	11.0	31
FN borosilicate	Centerless ground	14.8	43
Pyrex	-	-	64

For the purpose of long-term prediction a simple calculation of the time to failure at zero applied stress is given as  $5 \times 10^6$  years from a  $1 \mu\text{m}$  crack which determines  $t_{1/2}$  to be 2.14 seconds in water based on the formula of Wiederhorn and Bolz. (85,91) Various assessments at different stress levels and environmental conditions are possible and this will be a future research topic. In the above equations, the stress term can be converted into a fracture mechanics term by simple substitution resulting in a similar expression.

In practical design, a proofing test is used, and the time to failure,  $t_f$ , is usually expressed as

$$t_f = \sigma_a^{-2} f(\sigma_p/\sigma_a)$$

where  $\sigma_a$  is the service load,  $\sigma_p$  is a proof test load, and  $f$  is determined from measurements of  $K_{IC}$ , the critical stress intensity, and from crack growth data. (92-94) The data for borosilicate crown glass II is shown in Figure 3.2.

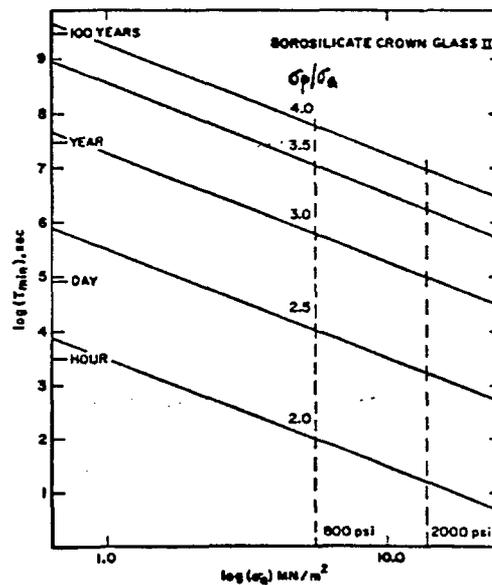


Figure 3.2 Proof test diagram for borosilicate crown glass II; minimum time to failure,  $T_{min}$ , given as a function of service stress,  $\sigma_a$ , and proof test ratio,  $\sigma_p/\sigma_a$ . (92,94)

From the practical viewpoint of a laboratory test, the critical stress intensity  $K_{IC}$  gives the material capability to carry a load in the presence of a given size of notch, or some other form of flaw or defect. The critical stress intensity factors for borosilicate glasses in vacuum are shown in Table 3.2

Table 3.2

Critical Stress Intensity Factor  $K_{IC}$  ( $MN/m^{3/2}$ ) of Borosilicate Glass<sup>(94)</sup>

Glass	Vacuum, DCB* No Preheat	Vacuum, DCB Preheat 300°C for 30 min.	Vacuum 3 Point Bend, No Preheat	Dry, N <sub>2</sub> Gas <0.02% RH
Borosilicate	0.760±0.007	0.770±0.012	0.777±0.032	0.764±0.008
Borosilicate Crown, I	0.862±0.032	0.927±0.010	0.842±0.007	--
Borosilicate Crown, II	0.866±0.001	0.879±0.034	0.904±0.014	--

\*DCB: Double Cantilever Beam.

However, when we consider geologic time periods, it is probable that cracking may develop even in the absence of applied stress (see Equation 6) during the corrosion process. One such example is shown in the study of cracks induced in a stress-free alkali silicate bottle after a few weeks exposure to water.<sup>(95)</sup> Such failure possibility can always take place for all glasses over geologic time.

The static fatigue model should eventually include the effects of surface stress caused by surface crystallization, hydration, or spalling which will also lead to crack propagation during the corrosion process. Therefore, the realistic prediction of time to failure will be much more complicated than the above simple equations which were derived from fracture mechanics and are basically empirical in nature.

### 3.4 Effects of Environmental Interaction

#### 3.4.1 Solution pH

It was determined that the pH of the aqueous environments has a significant effect on the strength of glass. In high pH solutions (above 13), the strength of glass was greater, while in low pH solutions (below 1), the strength was less than in neutral solutions. In strong alkali solutions, samples will not be susceptible to cracking when the corrosion rate proceeds

faster than the crack velocity.<sup>(95)</sup> In the middle range of pH, the strength is nearly constant. For silicate glass, the slope of the crack velocity versus stress intensity factor was found to decrease as the pH increases. Wiederhorn<sup>(87)</sup> rederived the crack velocity equation in the Charles and Hillig model, including  $[\text{OH}]^-$  ion concentrations, and found that the velocity is proportional to the nth power of the  $[\text{OH}]^-$  ion concentration.

When water is the corrosive agent, the effect of a wide pH variation is important since the crack tip solution is rapidly modified by the glass and contains significant concentrations of elements that are normally present in the glass composition. Wiederhorn<sup>(96)</sup> further stated that high alkali glasses result in basic solutions at the crack tip, whereas low alkali glasses have crack tip solutions that are mildly acidic. This local pH change is determined by a dynamic balance between the ion-exchange and ion-diffusion processes. This local pH influences the slope and the shape of the universal fatigue curves.

#### 3.4.2 Humidity

Humidity will hydrate the surfaces of some glasses causing them to swell, thus creating local stresses at a flow tip which will propagate cracks. The crack velocity is found to be proportional to the relative humidity by a theoretical analysis.<sup>(97,98)</sup> The time to failure for older glass was found to be an inverse exponential function of the relative humidity.<sup>(99)</sup> These are valid when other parameters governing the crack growth or the time to failure are fixed. Quantitative data for borosilicate glasses are not available at the present time.

#### 3.4.3 Temperature and Pressure

Glasses of poor chemical durability tend to crack at lower temperatures; concomitantly, the reverse is true at very high temperatures. The crack growth velocity and the time to failure have been expressed in an Arrhenius-type equation relating to temperature. For borosilicate glass, the activation energy for the crack velocity is reported in the previous section on fracture mechanics. The characteristic time to failure,  $t_{1/2}$ , is simplified to be a linear function of temperature.<sup>(85)</sup>

As for pressure dependency, high pressure is known to have no effect on static fatigue in the range of 6 to 7 Kbar.<sup>(100)</sup>

#### 3.4.4 Glass Composition

Both the crack velocity and the time to failure change as the composition changes.

Systematic studies on composition effects or data pertaining to borosilicate glass per se are not available at the present time.

### 3.4.5 Flaws

The delayed failure curves for a number of glasses were quite sensitive to surface finish. Generally as the flaw size increases, the time to failure decreases. There is no report on the limitation of flaw size, below which no failure occurs. For optical fiber glass, the failure origin was found even though flaw sizes are much less than  $1 \mu\text{m}$ .<sup>(98)</sup> Since  $t_{1/2}$  is also a function of flaw size, universal fatigue curves are obtained when the time to failure is normalized in most cases. The fracture mechanics study illustrates the quantitative prediction of the dependency of flaw size on the time to failure or  $t_{1/2}$ .

### 3.4.6 Microstructure and Plastic Deformation

Phase separation is reported to increase the crack growth rate.<sup>(98)</sup> The plastic deformation is believed to play no role in the fracture process. However, very little quantitative data is available concerning these properties.

Static fatigue data for nuclear waste glass are not available at the present time. Several laboratories, including the National Bureau of Standards, have recently begun formal studies on this subject.

#### 4. RADIATION EFFECTS

This section will briefly summarize the anticipated radiation effects on leaching and overall integrity of glass based on experimental work on commercial and nuclear waste glass. A more detailed review is due to appear in the BNL literature.<sup>(20)</sup>

In waste glass, alpha, beta, gamma-rays, and transmutation effects are expected to exist.<sup>(28)</sup> Recently, Walker, et al.<sup>(101)</sup> reported on a preliminary study involving borosilicate glass leaching during  $^{60}\text{Co}$  gamma,  $^{244}\text{Cm}$  alpha, and  $^{90}\text{Sr}$  beta radiation. Leach rate was increased within a factor of 2 by gamma radiation presumably due to the leachant pH change by radiolysis, while no significant effects were observed for alpha or beta radiation. To date, transmutation effects on glass leaching have not been reported in the literature. Studies on crystalline waste forms<sup>(102)</sup> seem to indicate that the effect may not be significant. Indirect effects involving differential swelling and compaction have been observed in partially devitrified glass by alpha and gamma radiation leading to microfracturing. The concomitant increase of surface area will enhance the leach rate quite significantly<sup>(103)</sup>. Similar effects are expected as a result of transmutations. The concentration of transmuted atoms may be large enough to form a second phase causing stress generation at the interface. No experimental evidence has been reported to date on this topic.

In a design utilizing commercial glass in a sacrificial capacity to encapsulate the nuclear waste glass, beta and gamma radiation effects are anticipated. Following the results of Walker, et al.,<sup>(101)</sup> it appears that only the gamma radiation would affect the leach rate. An indirect effect may involve stress generation between the sacrificial layer and the waste glass from differential compaction and swelling. This stress may lead to microfracturing resulting in increased leach rate due to increased surface area.<sup>(103)</sup>

Dose rates under repository conditions are assumed to be generally slower than under laboratory conditions reducing the above mentioned radiation effects. Given the limited experimental data, it becomes quite difficult to assess the effects of radiation on the integrity of glass over geological time. However, we feel that the radiolysis effect is quite minor and the fracture process can be avoided by a proper design of the waste form<sup>(103)</sup> which would preserve the integrity even in the presence of radiation.

## 5. LONG-TERM PREDICTION MODELS

All the efforts reviewed up to this point were aimed at predicting the durability of glass over geological time. The numerous complications and uncertainties in the preceding sections suggest that it is quite premature to generate a comprehensive model for prediction. Nevertheless, researchers have attempted to develop a method for long-range prediction of the durability of nuclear waste storage materials based on several hypotheses.

Hench<sup>(4)</sup> emphasized a graphical method based on the analyses of laboratory tests, field tests, and natural analog materials by plotting material loss through leaching as a function of time. The best and worst cases are used for the upper and lower limit of the plot. For example, the accelerated leach rate by hydrothermal conditions is a factor controlling the worst case. It was admitted, however, that there are so many uncertainties involved, it is almost impossible to construct any specific chart at the present time. For instance, a study of natural analogs, especially in relation to laboratory tests, has only recently begun. Several scenarios of film dissolution and rupture behavior presented by workers at Catholic University<sup>(15)</sup> offer additional proposals for the prediction of long-term durability.

Current attempts at modeling face severe shortcomings by their recourse to a limited number of variables. As shown in the previous sections, the interacting variables are complex and require a more sophisticated and realistic treatment if they are to offer any predictive advantage at all.

## 6. CONCLUSIONS AND RECOMMENDATIONS

We have reviewed various chemical and mechanical processes for the degradation of glass. Such processes are often translated into formulas or models for the prediction of long-term durability. Attempts have been made at constructing predictive models for borosilicate glass in a water environment based on experimental data. Since current efforts in this area are valid only under very limited circumstances it is inevitable that we conclude our review on a qualitative note.

From the experimental results on the leaching of binary systems, the diffusion controlled dealcalization is predominant in the beginning with a square root time dependence while the appearance of network dissolution occurs with a linear time dependence following the diffusion process. However, the development of the time laws for this process is still too idealized and a linear extrapolation of those kinetics to geological time is, therefore, quite oversimplified at present. In the case of multicomponent systems even such simple kinetics are not currently available.

Solution and environmental variables such as temperature and pressure will have a direct effect on the durability of glass. As dealcalization proceeds, the nature of the solution will change. The solution composition effects are difficult to discern since these are interrelated to pH change and passive film formation at the glass surface. Typical reactions in simple systems involve silica network dissolution in high alkaline solutions and lower leach rates in neutral and acidic environments. Multicomponent glass systems also exhibit greater durability in acidic environments. Changes in pH, precipitation, and the effects of erosion resulting from variations in flow rates may result in unpredictable leach rates. The single activation process, observed in many commercial and nuclear waste glasses, offers a method of accelerating conditions at high temperatures to simulate long-term corrosion effects. For hydrothermal conditions, the alteration product resulting from glass-solution interaction is one of the most important variables determining the leach rate. A thorough understanding of the role played by the altered zone is needed in order to adequately identify the mechanisms involved in the corrosion process.

Glass composition is one of the most important factors determining the leach rate. Generally, network formers and divalent modifiers increase durability while monovalent modifiers have the opposite effect. The effects of phase separation on leaching is dependent on the microstructure and can either enhance or retard durability. The ratio of solid surface area to solution volume is another important parameter effecting leach rates. However, the difficulty in the determination of the total surface area makes the exact formulation of this parameter extremely difficult. As parameters having secondary effects on the leaching process, partial devitrification, internal stress, surface roughness, and local inhomogeneity contribute to changes in the leach rate. No quantitative data on the contribution of these parameters are available at the present time.

Toxic radioisotopes may escape from the waste form by solid state diffusion. Tabulations of gas and ionic diffusivity in glass indicate that such events are very unlikely under repository conditions.

In glass, local corrosion is not any more severe than general corrosion. Static fatigue, however, should be recognized as an important mode of disintegration over geological time. From the well-defined fracture mechanics, it is known that there is a fatigue limit for borosilicate glass below which no cracking occurs; however, changes at the microstructural level may modify the fatigue limit hypothesis. Modifications may arise due to surface stress, solution pH, humidity, temperature, pressure, compositional and microstructural inhomogeneity.

Radiation would probably not affect the leach rate by more than one order of magnitude as a result of radiolysis. An indirect effect such as microfracturing may be avoided by a proper design of the multibarrier glassy waste form.

Typical values for the dissolution rate of waste borosilicate glass range from  $10^{-7}$  to  $10^{-4}$  g/cm<sup>2</sup>-d, varying depending on the component. From the data at hand on the chemical and mechanical aspects of glass durability, and given an adequate design incorporating sacrificial layers and a proper burial site selection, waste form integrity, at least for the first thousand years, is achievable. It is still premature to attempt quantifying material released from glass over geological time since major uncertainties exist in the identification of the various mechanisms involved in glass leaching. Several research topics which would contribute to our understanding of long-term corrosion are presented below:

- Study the effects of groundwater ions on the selective leaching and passive film formation.
- Study pH effects on nuclear waste glass--seek to explain why acidic solutions affect leaching in binary glass differently from leaching in multicomponent systems;
- Study the flow rate effect in multicomponent systems thoroughly, especially the relative change of solution pH, reprecipitation, and passive film formation;
- Verify the single activated process by the measurement of leach rate as a function of temperature systematically for multicomponent systems;
- Study the surface chemistry of the alteration zone during leaching, especially during hydrothermal reactions. Surface-sensitive tools such as ESCA and AES are useful and should be adopted;
- More sensitive analytic tools, such as neutron activation analysis, should be used in the analysis of the leachate;
- Study the optimization in tailoring the glass composition for best leach resistance along with a formulation of the mechanisms involved, especially in multicomponent systems incorporating nuclear waste;

- Study the optimum microstructure for high leach resistance based on the principle of phase separation;
- Develop valid means of defining and measuring the surface area of powdered and cracked samples. Local pH change and corrosion cell formation in powdered samples should be thoroughly understood;
- Partial devitrification, surface roughness and local inhomogeneity should be studied more quantitatively;
- Measure ionic and gas diffusivity in glass at ambient temperatures; especially the diffusivity of fission products in nuclear waste glass;
- Study the wet-dry cycle effect on glass and compare the results to natural and archaeological analogs;
- Use a more mechanistic approach in understanding static fatigue--the effects of surface stress on crystallization is one example as opposed to relying on the well defined artificial stress intensity. More quantitative studies of the effects of pH, humidity, temperature, pressure and glass composition are needed, especially in the area of nuclear waste glass development;
- In radiation effects,  $\alpha$ -radiolysis, and radiation induced cracking and pH change should be studied.
- Study of natural analogs and ancient glass requires a more systematic approach if they are to offer insights into long-term durability;
- More sophisticated and comprehensive modeling of glass corrosion processes are needed. Computerized code generation may be a necessary step in the assessment of the complex processes and in the area of long-term prediction of glass durability.

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APPENDIX R

MECHANISMS FOR TRANSPORT OF  
RADIONUCLIDES FROM THE WASTE BACKFILL

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## 1.0 INTRODUCTION

The waste package must be designed to contain all radionuclides during the 1000 years when thermal effects, related to the decay of short-lived nuclides are most severe. During the rest of the regulatory period, radionuclide release from the waste package must be less than 1 part in  $10^5$  of the maximum amount present in the waste form. The role of the packaging in retarding the movement of radionuclides from the waste form, through the waste package, to the near-field environment is an important element of the waste package design. An understanding of the potential

transport and retardation processes is necessary for predictions of the flux of radionuclide contaminants from the waste package. The release rate will depend <sup>in part</sup> upon the properties of the radionuclide species produced during degradation and of the waste form, the properties of the packing material. In this appendix, the <sup>fluid flow,</sup> potential importance of Fickian diffusion, thermodiffusion, and colloid production <sup>transport</sup> to the waste elements through the packing material will be discussed.

1-2. REGULATORY FRAMEWORK

## 2.0 DISCUSSION

### 2.1 GENERAL

For this discussion, the general topic of radionuclide transport through the packing material will be divided into three distinct areas: (1) generation of <sup>aqueous or colloidal</sup> radionuclide species by degradation of the waste form, (2) transport of these species by fluid flow or <sup>Fickian diffusion or thermo</sup> diffusion and (3) retardation of the species by processes such as sorption, chemical substitution, precipitation and Insert 1 ultrafiltration. Three specific questions that are relevant to predictions of the <sup>radionuclide</sup> release rate will be addressed in this section. These are:

# Inset 1

The theoretical principles and experimental methods <sup>and operation</sup> of solubility determination are discussed in Appendix U. The hydrothermal stability of the boronite / basalt packing material is discussed in Appendix —. The resistance of the packing to mechanical degradation modes such as cracking is discussed in Appendix —.

1. Under what hydraulic conditions will transport by diffusion dominate radionuclide migration through the backfill?

(radionuclide release is significantly by <sup>affected</sup> the production and transport of <sup>radionuclide</sup> colloids or pseudo colloids in the waste package?)

3. What are the potential retention times of radionuclides within the packing material after release from the waste form?

Which radionuclides will decay to relatively low levels during this time?

## 2.2 ISSUES

### 2.2.1 Fluid transport in the packing.

#### 2.2.1.1 General principles

The magnitude of fluid transport through the packing material will be determined in part by the hydraulic conductivity,  $K$  (cm/s) of the material. The conductivity of the packing is related to the volumetric flux,  $Q$  (cm<sup>3</sup>/s) and the hydraulic gradient,  $i$  (cm/cm) by Darcy's law.

$$Q = -KiA \quad (1)$$

where  $A$  is the surface cross sectional area perpendicular to the direction of flow.

(Freeze and Cherry), The hydraulic conductivity can also be related to more fundamental properties of the packing

temperature, fluid composition and hydraulic gradient.  
These relationships are discussed in Section 2.4.1

by the following expression

$$K = k\rho g / \mu \quad (2)$$

where  $k$  is the permeability ( $\text{cm}^2$ ),  $g$  is the gravitational acceleration and  $\rho$  and  $\mu$  are the fluid density ( $\text{g}/\text{cm}^3$ ) and fluid dynamic viscosity ( ) respectively.

The hydraulic conductivity of bentonite clay is also ~~inversely~~ related to the compaction. Values of  $K$  for potential packing materials can be density or swelling pressure. Found in

Appa. et al., Westick et al., Meretnickes et al., Bida and Eastwood, and Smith et al.  $\rho$  of compaction density of  $2.1 \text{ g/cm}^3$ , Westick measured hydraulic conductivities  $5 \times 10^{-13} \text{ cm/s}$ ,  $7 \times 10^{-12} \text{ cm/s}$  and  $1.5 \times 10^{-12} \text{ cm/s}$  for

pure sodium bentonite, a 25% clay / 75% sand mixture and a pure calcium bentonite respectively. The measured values of  $K$  were constant over the range of hydraulic gradients used ( $1.2 \times 10^4$  to  $7.5 \times 10^5$ ). These values are consistent with data presented in the other aforementioned references.

### 2.2.1.2 Applications to Waste Package Performance

The design life of the packing material can be divided into two periods (Bida, G). In the first period, the bentonite is not water-saturated. During this time, water is excluded from the container but an appreciable <sup>water</sup> flow rate occurs toward the waste until 100% saturation is reached. The length of this time period is a function of several variables and is impossible to predict with available data (Bida, G).

The saturation time will depend upon the hydration rate of the dry bentonite.

Based on preliminary data, ONZ has estimated that several thousand years would be required for water to penetrate and saturate 20 cm of bentonite

(Wheelwright, E. in Bida, G.), Smith gives a conservative estimate of 15-50 years for saturation of a 0.3m-thick packing assuming a hydraulic gradient of 10 MPa. and neglecting the effects of the swelling pressure.

During the second time period, after saturation of the packing, movement of water through the ~~packing~~ waste package will be controlled by primarily within by the hydraulic gradient of the repository and the hydraulic conductivity of the packing material.

Assuming conservative values for these parameters, Bida et al calculated that <sup>would be</sup>  $1 \times 10^5$  years, required for a volume of ground water equal to the volume of a typical waste package to contact the container. It has been shown

(Bida, B and Apps, J) that ~~transport by~~ <sup>for reasonable</sup> diffusivities, <sup>a diffusion dominates</sup> mass transfer through the packing ~~is~~ when the hydraulic conductivity is less than  $10^{-11}$  cm/sec, ~~is~~ <sup>For</sup> expected at the BWIP site ( $5 \times 10^{-4}$  to  $5 \times 10^{-5}$ ), the very low hydraulic gradients, calculated

break-through times for radionuclides in a clay barrier are independent of the fluid flow velocity. <sup>(if the packing maintains its mechanical integrity)</sup> Thus, radionuclide transport through the packing will

occur by diffusion through an effectively stagnant fluid within the interstitial pores of the clay.

### 2.2.2. Diffusional Transport

#### 2.2.2.1 General principles and definitions of terms

• Chemical diffusion : a solute - mixing process in which solute ~~is~~ species migrate <sup>from</sup> regions of high chemical potential (~~concentration~~ <sup>thermodynamic</sup> activity) to low chemical potential (<sup>thermodynamic</sup> activity). The flux, and concentration of the solute can be described by Fick's laws

of diffusion as described below.

insert 2

• Diffusivity, <sup>(D)</sup> : a constant ~~is~~ <sup>called also the diffusion constant</sup> ~~which~~ <sup>aqueous</sup> characteristic of an species in a

## Inset 2

- Fick's Laws of diffusion : basic equations describing <sup>solute</sup> flux and concentration under flow regimes where transport diffusion is important. For one-dimensional

$$F = -D \frac{\partial C}{\partial x} \quad (\text{Fick's First Law}) \quad (3)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (\text{Fick's Second Law}) \quad (4)$$

where  $F$  <sup>and</sup>  $C$  are the solute flux, <sup>and</sup> concentration respectively,  $x$  is the direction of transport  $t$  is time and  $D$  is the diffusivity. Although equations 3 and 4 are written in terms of  $D$ , the diffusivity in solution, the equations for diffusion in a porous media contain terms for properties of the clay

Insect 2 continued

11b

the  
such as tortuosity, porosity, and sorption  
distribution coefficients.

fluid phase. (units:  $\text{cm}^2/\text{s}$ ).

- Apparent diffusivity,  $(D_a)$ : a diffusion constant ~~for~~ for aqueous species in a porous matrix which includes the effect of retardation. (units:  $\text{cm}^2/\text{s}$ )

- Retardation Factor: the relative velocities of the contaminant and ground water.

For systems in which sorption is

reversible,  $R = 1 + K_d \rho / \phi$  where

$R$  is the retardation factor,  $K_d$  is

the equilibrium sorption distribution

coefficient,  $\rho$  is the bulk density

and porosity respectively

of the clay matrix, and  $\phi$  is the

(t)

- Retention time,  $t_r$ : in a diffusion

experiment, the time required for

breakthroughs to occur across a barrier.

For a barrier thickness of  $z$  (m), the  
retention time, <sup>in a diffusion process</sup> would be given by

$$t = 0.1z^2/D_a$$

(Torstenfelt, P. 1982b). Breakthrough is defined to occur when the concentration outside the barrier reaches a certain fraction (commonly 1% or 5%) of the concentration at the contaminant source.

- Thermodiffusion (Soret effect): a transport process whereby aqueous species migrate down a thermal gradient.

### 2.2.2.2. Applications to Waste Package Performance

An equation describing the transport of a radionuclide through a homogeneous packing barrier in one dimension can be written as

$$\frac{D}{R} \frac{\partial^2 c}{\partial x^2} - \frac{v}{R} \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t} + \lambda c + \text{reaction terms}$$

where  $v$  is the interstitial fluid velocity,  $\lambda$  is the radionuclide decay constant and  $R, D, c, x$  and  $t$  are defined in

Section 2.2.2.1. The reaction terms include expressions for production or consumption of the radionuclide by precipitation, dissolution, irreversible sorption or substitution, ultrafiltration, and radioactive decay of parent nuclides.

## 2.4 METHODS

### 2.4.1 Hydraulic Conductivity

Test methods to determine <sup>the</sup> hydraulic conductivity of bentonite clays as functions of swelling pressures, compacted density and hydraulic head are described in Westrick, J;

Bida G. and Pusch, R. In experiments

performed at PN2 (Westrick, J.) the permeating fluid is pumped <sup>under high pressure</sup> into a permeability cell which contains a column of compacted, powdered

packing material. ~~After flowing through the column,~~

The fluid is collected in a preweighted vessel after it has flowed through the column.

The volumetric flow rate is determined by weighing the effluent as a function of time,

The hydraulic conductivity <sup>K</sup> and intrinsic

permeability  $k$ . are determined from equations

(1) and (2) respectively.

The hydraulic conductivity of the packing is dependent upon compaction density, temperature and hydraulic gradient.

The compaction density in turn ~~is dependent~~<sup>is</sup> a function of the compaction pressure and the initial water content. During the first several hundred years after repository closure, the water content of compacted bentonite in the packing may be close

to zero because of the thermal environment. Water will only be present as vapor in the outer layers of the packing in the waste package. The compaction density

therefore, will be a strong function of time as the waste package cools and the

packing rehydrates. <sup>Future BWIP</sup> investigations of the performance of the packing material should

examine the  $\phi$  of packing material  
capaciton density, as a function of rehydration  
as water vapor returns to the liquid  
state (Bida, G.)

The dependence of hydraulic conductivity  
on hydraulic gradient is discussed in  
Westrick, J. and Bida, G. and Pusch, R.  
The permeabilities  
of swelling clays, such as bentonite, increase  
as the hydraulic gradient is increased. Deviations  
from Darcy's law are observed at very low  
hydraulic gradients. Values of hydraulic  
conductivities reported from <sup>the high-gradient experiments</sup> PNL may ~~therefore~~  
<sup>therefore,</sup> lead to overestimates of flow within the  
BWIP waste package. The dependence of  
hydraulic conductivity on temperature  
can be related <sub>in part</sub> to the temperature

dependences of the compactum density, fluid density, dynamic viscosity, (cf. equation 2) and diffusion rates.

Plans for investigations of hydraulic conductivity as a function of temperature are discussed in Bida, B. The effect of the variation of other environmental parameters such as ground-water composition, redox potential and radiation field should also be considered in future studies of fluid flow through packing material.

Issue No. 2.1

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What are the possible mechanisms by which water will penetrate the packing material around containers?
3. Importance of the Issue to Repository Performance

Penetration of the packing material around the container by groundwater may result in contact of the waste container with the groundwater. In turn, contact of the waste container with groundwater may lead to corrosion, thus compromising the integrity of the container and of the waste form within. Movement of water through the waste package provides a potential release pathway for radionuclides.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

§ 60.113 Performance of particular barriers after permanent closure.

(a) General provisions.

- (1) Engineered barrier system

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) Containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste package will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release rate of any radionuclide following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total annual release at 1,000 years following permanent closure.

#### Design Requirements for the Waste Package

§ 60.135 Requirements for the waste package and its components.

(a) Waste package design requirements for high-level waste.

(1) Packages for HLW shall be designed so that the in-situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.

(2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge, With Analysis of Uncertainties

Penetration of the packing material by water may occur as a result of an increase in hydraulic conductivity caused by one or more of the following chemical degradation mechanisms (BNL-NUREG-31770, 1982):

- loss of hydrothermal stability.
- aging.
- selective dissolution on leaching of the packing material matrix.
- radiation effects, including radiolysis.

The hydrothermal stability of the packing material is the principal cause of concern.

Water may also penetrate the packing material by means of the following mechanical failure mechanisms (BNL-NUREG-31756, 1982):

- fracturing
- embrittlement
- liquefaction
- hydrologic erosion

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

Further investigation is needed of the changes in the hydraulic conductivity of candidate packing materials resulting from the chemical degradation mechanisms listed in (5), above, in the 100° to 300°C temperature regime at pressures of 300 bars with the dissolved solids concentrations, the Eh, and the pH of the simulated groundwater at their expected values under repository conditions. Also, the mechanical failure mechanisms listed in (5), above, need further study under expected repository conditions. (For example, it is not clear if such mechanical failure mechanisms occur under expected repository conditions.) Because irreversible microstructural changes may occur in the

packing material as a result of exposure to repository conditions, the effects of the history of the material as well as the effects of the conditions at the time of testing should be addressed. (For example, how does prior exposure of the material to 300°C at 300 bars for some specified time period affect the hydraulic conductivity later at 100°C at 300 bars?)

7. Summary of the Planned Approaches to Testing, Tests, Test Methods and Investigations to Provide the Information Needs of (6):

The present issue is addressed by the following Work Element in the SCR:

W.1.15.B: Define the characteristics of the packing materials required to retard the flow of groundwater to the container. Identify packing materials with these characteristics.

Measurements of the hydraulic conductivities, swelling pressures, and mechanical strengths of various unspecified basalt/bentonite mixtures are planned. These properties will be measured as a function of temperature and density. The dependence of these properties on moisture content and grain size must also be determined. These data will be used to verify the licensability of the reference waste package packing material mixture of 25% bentonite/75% basalt by volume. Other potential mixtures (for example, crushed basalt and sand) will also be investigated.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

The conditions under which the measurements described in (7), above, will be performed are not well defined in the discussion of Work Element W.1.15.B in the SCR. Pressure is not explicitly mentioned as an important variable, <sup>nor</sup> is any mention made of the use of simulated basalt groundwater at the appropriate pH and Eh as the permenting fluid. Temperatures of up to 300°C at pressures of 300 bars (maximum lithostatic pressure) in the presence of simulated groundwater are discussed in connection with other Work Elements, for example, W.1.16.B. Measurements of the wetting of an initially dry packing material

are not explicitly noted in the SCR, and measurement of the hydraulic conductivity as a function of the hydraulic gradient are not discussed. It is possible to conduct measurements of the penetration of packing materials by water under repository conditions in autoclave systems.

References:

1. BNL-NUREG-31756, "Testing for Mechanical Failure of Bentonite in a Discrete Backfill for Basalt and Salt Repositories, Draft Report," B. Siskind, Brookhaven National Laboratory, August 1982.
2. BNL-NUREG-31770, "Chemical Failure Modes of Bentonite and Zeolites in Discrete Backfill for Nuclear Waste Repositories, Draft Report," D. Eastwood, Brookhaven National Laboratory, August 1982.
3. NUREG/CR-2759, "Discrete Backfill Testing Required to Demonstrate Compliance with 1000-year Radionuclide Containment," A. Bida and D. Eastwood, Brookhaven National Laboratory, May 1982.
4. NUREG/CR-2780, "Near-Field Repository Conditions in Basalt and Salt," B. Siskind and D. Hsich, Brookhaven National Laboratory, May 1982.
5. NWTs-16, "Draft Interim Reference Repository Conditions for a Nuclear Waste Repository in Basalt," Reference Repository Conditions Interface Working Group, National Waste Terminal Storage Program, ONWI, DOD, September 1981.
6. RHO-BWI-ST-7, "Engineered Barrier Development for a Nuclear Waste Repository in Basalt: An Integration of Current Knowledge," M. J. Smith and others, Rockwell Hanford Operations, May 1980.

Issue No. 2.2

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington.

2. Statement of the Issue: To what extent over time will groundwater flow, temperature, or other effects change the ability of packing materials to control flow through those materials? What chemical and physical changes are possible? What are the chemical and physical properties?

3. Importance of the Issue to Repository Performance: Changes in the chemical and physical properties of the packing material may affect the ability of these materials to control the flow of groundwater and radionuclides through the waste package. Contact of the waste container with groundwater may compromise the integrity of the container and of the waste form within movement of water through the waste package provides a potential release pathway for radionuclides.

4. Portions of 10 CFR 60 that are Directly Connected to the Issue:

§ 60.113 Performance of particular barriers after permanent closure.

(a) General provisions.

(1) Engineered barrier system

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (a) Containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (b) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste package will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release rate of any radionuclide following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total annual release at 1,000 years following permanent closure.

#### DESIGN REQUIREMENTS FOR THE WASTE PACKAGE

§ 60.135 Requirements for the waste package and its components.

(a) Waste package design requirements for high-level waste.

(1) Packages for HLW shall be designed so that the in-situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.

(2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge, With Analysis of Uncertainties

Reduction of the ability of the packing material to retard the flow of water and radionuclides may result from a variety of chemical and physical changes:

- loss of hydrothermal stability
- aging
- decrease in sorptive capacity by chemical reaction or poisoning
- selective dissolution or leaching of the packing material matrix
- radiation effects, including radiolysis
- fracturing
- embrittlement
- liquifaction
- hydrologic erosion.

Although such degradation mechanisms have been characterized to varying degrees, much of this information has been obtained under conditions not typical of those expected in the BWIP repository (see NUREG/CR-2755, BNL-NUREG-31756, and BNL-NUREG-31771, 1982).

Several chemical and physical properties of the packing material which are of primary importance in the ability of the packing material to control flow are affected by the above changes. These properties are the hydraulic conductivity, swelling pressure, plasticity (on extrudability), density, diffusion coefficient, sorptive capacity, and ion exchange capacity.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

Because the packing material will experience a temperature cycle from an initial repository ambient temperature (60 to 70°C) to as high as 250-300°C and then a slow return to ambient while the pressure increases to 300 bars, the temperature dependence of the chemical and physical properties on which the packing material attributes are based must be known over a temperature range of 60 to 300°C at 300 bars of pressure. The effects of groundwater

composition, Eh and pH on the chemical and physical properties of the packing material must also be known. (NUREG/CR-2755, 1982, Section 2.2.1). Very similar information needs have been identified in the SCR (Section 15.3).

- Thermal stability of potential packing materials (primarily basalt/bentonite mixtures) in the temperature range 150° to 300°C at 300 bars for up to 6 months.
- Mineralogical and chemical characterizations of alteration phases for basalt and packing materials under expected repository conditions (150° to 300 bars, simulated groundwater chemistry, expected Eh and pH).
- Effects of radiation on the above measurements.
- Rates of the above processes.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

Approaches to the present issue are implicitly addressed by the following work elements in the SCR:

- W.1.16.B Define the characteristics of the packing material required to reduce the rate of radionuclide release from the waste package. Identify packing materials with these characteristics.

Hydrothermal experiments are being conducted under site-specific conditions in the range of 150 to 300°C to determine the thermal stability limits of packing materials. The effects of dehydration on the structural stability of hydrated candidate packing materials (for example, smectite clays, zeolites) are being investigated. On the basis of data being generated currently, packing material mixtures will be chosen and flow-through experiments completed under repository conditions to measure radionuclide transport through a saturated

packing material. These data will then give an indication of whether radionuclide transport rates [and the flow of groundwater] can be controlled satisfactorily by the packing materials.

- W.1.12.A Determine the extent to which the interaction between the container materials, waste form, packing material, and host rock in a saturated environment results in retardation of radionuclides.

Hydrothermal-interaction studies of barrier materials are to be carried out with controlled experimental parameters over the relevant range of repository conditions. Temperatures should range between 100° and 300°C, with a total pressure of 300 bars (full lithostatic pressure). Periodic sampling of the groundwater solutions under test conditions is necessary to determine the rate of approach to steady-state solution composition. Hydrothermal hot-cell testing of engineering-scale waste packaged will be scoped to measure critical interactions in a radiation field.

- W.1.3.A Determine the effect of the waste package radiation environment on the near-field geochemistry, waste package, and barriers material performance.

Two methods are planned for investigating the effect of radiation on stability and degradation modes of barrier materials:

- (1) Imposition of a radiation field on standard container and packing material testing apparatus.
- (2) Inclusion of barrier materials with radioactive waste forms inside hydrothermal autoclaves of a hot-cell facility.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

The planned approach described in (7), above, is relatively complete. Details of the proposed studies are not given in the SCR, but such studies are well

within the state of the art with respect to feasibility. Measurements combining the features of all three work elements should also be carried out, that is, a flow-through experiment under expected repository conditions including interaction between the waste package components under hydrothermal conditions in a radiation field. Such a study would, in effect, be a waste package simulation. The studies outlined in (7), above, from the SCR, as well as the waste package simulation just mentioned, should be carried out for extended periods of time, at least the six months noted in (6) above and longer, if possible. (There are some minor problems with the Work Elements. For example, no external pressure is mentioned in W.1.16.B. Also, the lower limit of the temperature range is given as 150°C in W.1.16.B and 100°C in W.1.12.A. Probably, a better, more comprehensive lower limit would be 60°C as noted in (6), above, based on ambient repository conditions.

References:

1. BNL-NUREG-31756, "Testing for Mechanical Failure of Bentonite in a Discrete Backfill for Basalt and Salt Repositories, Draft Report," B. Siskind, Brookhaven National Laboratory, August 1982.
2. BNL-NUREG-31770, "Chemical Failure Modes of Bentonite and Zeolites in Discrete Backfill for Nuclear Waste Repositories, Draft Report," D. Eastwood, Brookhaven National Laboratory, August 1982.
3. NUREG/CR-2759, "Discrete Backfill Testing Required to Demonstrate Compliance with 1000-year Radionuclide Containment," A. Bida and D. Eastwood, Brookhaven National Laboratory, May 1982.
4. NUREG/CR-2780, "Near-Field Repository Conditions in Basalt and Salt," B. Siskind and D. Hsich, Brookhaven National Laboratory, May 1982.
5. NWTs-16, "Draft Interim Reference Repository Conditions for a Nuclear Waste Repository in Basalt," Reference Repository Conditions Interface Working Group, National Waste Terminal Storage Program, ONWI, DOD, September 1981.
6. RHO-BWI-ST-7, "Engineered Barrier Development for a Nuclear Waste Repository in Basalt: An Integration of Current Knowledge," M. J. Smith and others, Rockwell Hanford Operations, May 1980.

Issue No. 2.3.1

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What are the hydrothermal conditions with time at the surfaces of the waste form and container and within packing materials which influence property changes and radionuclide release?
3. Importance of the Issue to Repository Performance

The stability of a waste package component on exposure to liquid water at temperatures between about 50° and 400°C and at high enough pressures to keep the water in a liquid state is termed hydrothermal stability (BNL-NUREG-31770, 1982, p. 50). Hydrothermal stability is a primary consideration in any analysis of waste package performance because of the possibility of groundwater intrusion in the presence of radioactive decay heat under an external hydrostatic and/or lithostatic pressure. Loss of integrity of the waste package may result if any of its components have poor hydrothermal stability characteristics.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

§ 60.113

(a) Generation provisions.

(1) Engineered barrier system.

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) Containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered

barrier system shall be a gradual process which results in small fractional releases to the geological setting over long times.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste package will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release rate of any radionuclide following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total annual release at 1,000 years following permanent closure.

§ 60.135 Requirements for the waste package and its components.

(a) Waste package design requirements for high-level waste.

(1) Packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.

(2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength,

mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

The near-field temperature conditions for the undisturbed basaltic host rocks are relatively well defined, a range of 60° to 70°C having been given as a "reasonable estimate" for the Umtanum flow in the Groude Ronde formation. Estimates have also been made for the maximum temperature (300°C) and pressure (100 bars and 300 bars for the hydrostatic and lithostatic pressures, respectively, at a depth of 1000 m). The temperature will drop as the radionuclides in the waste decay, leveling off to the original temperature of the flow after about 1000 years. The pressure at the time of emplacement is close to atmospheric, but after repository closure the pressure is expected to increase over a unspecified time period to some value between the hydrostatic and lithostatic pressures. See NUREG/CR-2780 (1982) and the references cited therein, in particular RHO-BWI-ST-7 (1980) and NWTS-16 (1981) for further details.

6. Summary of Additional Information Needed to Resolve the Issue by the Time of Construction Authorization Application

Better definition of the near-field temperature and pressure characteristics as a function of time is needed and can be obtained only from an analysis of specific waste package designs within a well-characterized near-field repository environment. The thermal loading of the waste form and the thermal conductivity characteristics of the waste package components and of the host rock must be used to calculate the near-field temperature as a function of time. The swelling characteristics of the packing material upon exposure to water must be used to deduce the rate of approach to pressure equilibrium.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

Approaches to the present issue are simply addressed by the following work elements in the SCR:

W.1.2A. Determine conditions that affect design of waste packages, including thermal loading, mechanical loading, and chemical environment during...emplacement...and after repository decommissioning.

Thermal hydraulic models of the waste package, repository, and host rock will be used to estimate the time for migration of groundwater around and into the waste package. The results will depend on the specific repository and waste package designs selected, so the evaluations will be updated for the conceptual, preliminary, and final design phases.

W.1.12A. Determine the extent to which the interaction between the container materials, water form, packing material, and host rock in a saturated environment results in retardation of radionuclides.

Hydrothermal-interaction studies of barrier materials are to be carried out with controlled experimental parameters over the relevant range of repository conditions. Temperatures should range between 100° and 300°C at a pressure of 300 bars (lithostatic pressure). Hydrothermal hot-cell testing of engineering-scale waste packages will be scoped to measure critical interactions [identified in the hydrothermal interaction studies of barrier materials] between the several components of a waste package which incorporates a radioactive waste form. Test data will be reconciled with model predictions.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success

The two approaches outlined in (7), above, should together lead to a better definition of the hydrothermal conditions in the vicinity of the waste

package. The two planned approaches are not described in detail in the SCR and could not be at the present stage of waste package design. Feedback between the thermal hydraulic modeling and the hydrothermal-interaction studies will be necessary as part of the development of both the hydraulic modeling and the hydrothermal-interaction studies. The modeling and the hydrothermal-interaction studies are both feasible. The period of time over which the hydrothermal studies would be carried out is not given in the SCR.

References:

1. BNL-NUREG-31756, "Testing for Mechanical Failure of Bentonite in a Discrete Backfill for Basalt and Salt Repositories - Draft Report," B. Siskind, Brookhaven National Laboratory, August 1982.
2. BNL-NUREG-31770, "Chemical Failure Modes of Bentonite and zeolites in Discrete Backfill for Nuclear Waste Repositories - Draft Report," D. Eastwood, Brookhaven National Laboratory, August 1982.
3. NURC/CR-2759, "Discrete Backfill Testing Required to Demonstrate Compliance with 1000-year Radionuclide Containment," G. Bida and D. Eastwood, Brookhaven National Laboratory, August 1982.
4. NUREG/CR-2780, "Near-Field Repository Conditions in Basalt and Salt" and B. Siskind and D. Hgieh, Brookhaven National Laboratory, May 1982.
5. NWTs-16, "Draft Interim Reference Repository Conditions for Nuclear Waste Repository in Basalt," Reference Repository conditions Interface Working Group, National Waste Terminal Storage Program, ONWI, DOE, September 1981.
6. RHO-BWI-ST-7, "Engineered Barrier Development for a Nuclear Waste Repository in Basalt: An Integration of Curreng Knowledge," M. J. Smith and others, Rockwell Hanford Operations, May 1980.

Issue No. 2.4

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: What are the possible mechanical failure modes for the container?
3. Importance of the Issue to Repository Performance

The container is generally considered to be the most important engineered barrier with respect to containing radionuclides. Because of this a container which remains unbreached by mechanical failure modes for extended periods will allow in-situ radionuclide decay, and delay the onset of waste-form leaching. Thus, a container will be of significant importance with respect to defining the radionuclide source term.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

§ 60.113 Performance of particular barriers after permanent closure

- (1) Engineered barrier system

- (i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times.

5. Summary of the Present State of Knowledge, With Analysis of Uncertainties

A recent report by Soo and Brewster (BNL-NUREG-31774, 1982) shows that the mechanical failure of a HLW container is primarily dependent on the specific design, the temperature history and the mode of loading. Containers constructed of thick, ductile, high-strength alloys will be more resistant to mechanical failure; lower temperatures will increase the strength and also reduce the possibility of failure. (It should be noted that corrosion-enhanced mechanical failure such as stress corrosion cracking, is considered elsewhere.) With respect to the effect of stress state on the failure for a container, four (4) different loading conditions are of importance (a) failure from lithostatic/hydrostatic stresses, (b) failure from seismic activity, (c) failure from waste form swelling or internal gas pressurization and (d) failure from residual stresses.

In a sealed basalt repository a summary report by Siskind and Hsieh (BNL-NUREG-51548, Part 1, 1982) states that at a depth of 1100 m the hydrostatic and lithostatic stresses in basalt would be 11 and 33 MPa, respectively. Recent work shows that the horizontal component of the stress from the rock overburden could be as high as 66 MPa (Doe, ONWI-9(4), 1980). However, in the case of BWIP, bentonite packing material would exert an additional stress on the container when it swells through saturation with groundwater. This swelling pressure would be additive to the hydrostatic stress and the total effective hydrostatic stress on the container could be as high as 21 MPa. At a temperature of 300°C, there could be deformation of the low carbon steel container, especially in the void region adjacent to the waste glass surface. This would lead to creep or ductile failure of the container.

Seismic events in which hard rock masses could deform along linear faults were considered to be a source of high stress by Pusch (KBS Report, KBS-TR-22, 1977). His analysis showed that certain materials used in KBS container designs would not withstand shear stresses which could breach the container. He believed, however, that high strength materials could withstand mechanical failure provided packing materials were placed around the container.

Waste glass may suffer from irradiation induced swelling which will deform the type 304L stainless steel mold into which the glass is cast. However, a maximum volume increase of 1 percent is anticipated after 1000 years and this would be expected to cause deformation in the mold rather than the surrounding low carbon steel container in the BWIP design.

Residual stresses in the low carbon steel container are probably concentrated in welded regions. Although they may induce local deformation at 300°C due to stress relief effects, they do not appear to present a problem in the absence of an aggressive environment. Since the BWIP waste package is non-shielded, hydrogen will be generated by gamma radiolysis and this could lead to container failure.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

In order to successfully specify a mechanically-adequate container design the following additional data requirements will be required:

- (a) A conservative estimate of anticipated stress levels in the container system over the 1000 year containment period.
- (b) A specification of the maximum compressive stresses (vertical and horizontal) and likely shear modes acting on the container system over the 1000 year containment period.
- (c) Accurate estimates of the container temperature as a function of time.
- (d) A detailed description of waste package materials, geometries, and dimensions to determine stress-strain behavior under likely loading conditions.
- (e) Comprehensive information of creep and other mechanical properties for low carbon steel base and welded material for temperatures

between 80-300°C. Effects of hydrogen level on deformation behavior also need to be determined.

(f) Multicomponent stress analysis to determine how the waste form and packing material modify the loading and deformation of the container.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

The contents of Work <sup>Element</sup> ~~W1wmwnt~~ No. W.1.2.A <sup>purpose</sup> to address the evaluation of mechanical loads on the container but, as discussed in NRC Issue No. <sup>2.6</sup> ~~2-1-2-2~~, the actual plan for this effect does not seem to devote enough effort to this problem. There appears to be little description of the types of mechanical failure which could occur after repository closure, with the exception of stress-corrosion cracking and hydrogen embrittlement described in Work Element W.1.6.A. It is felt that some consideration should be given to specifying likely mechanical failure modes for breaking the container since the distribution and size of failed zones will determine the rates of release of radionuclides from the waste form.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

At present the definition of mechanical failure modes for the container are not adequately addressed in the SCR Work Element. It is recommended that this be carried out as a important priority since the types of failure will influence radionuclide release rates. If the waste package design and reporting conditions are well defined it is likely that the controlling failure mode can be identified, and verified by experiment and structural analysis.

References:

1. BNL-NUREG-31774, "Mechanical Failure Mode Data Requirements for TiCode-12 High Level Waste Container System (Draft Report), August 1982.
2. NUREG/CR-2780, "Near Field Repository Conditions in Basalt and Salt," Brookhaven National Laboratory Report, 1982.
3. ONWI-9(4), "Stripa In-Situ Stress Measurements," 1980.
4. KBS-TR-22, "The Influence of Rock Movement on the Stress/Strain Situation in Tunnels on Bore Holes with Radioactive Canisters Embedded in a Bentonite/Quartz Buffer Mass," 1977.

Issue No. 2.5

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What are the chemical and physical property changes in container materials and what are the resultant properties.
3. Importance of the Issue to Repository Performance

The container will be the principal component that restricts water from reaching the waste form. Since its chemical and physical properties will be altered by corrosion and mechanical failure, its impact on the rate of radionuclide release needs to be quantified.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

\$60.113 Performance of particular barriers after permanent closure

- (1) Engineered Barrier system

- (i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

The consequences of container corrosion and mechanical failure processes need to be evaluated insofar as they affect the behavior of adjacent waste package components. Several important factors concern their effect on the release of

radionuclides from the waste form, and packing material performance. In the one case, the rate at which repository water flows around the waste form depends on the corrosion/mechanical failure mode operating. For example, catastrophic cracking from hydrogen embrittlement would be expected to give water unlimited access to the waste form, whereas failure by a small number of corrosion pits may restrict the release of radionuclides. A scenario for the corrosion/mechanical penetration of the container will, therefore, be needed. With respect to corrosion of low carbon steel, voluminous oxide formation will inhibit heat transfer and may elevate the waste form temperature and enhance the leach rate. Together, the corrosion products and released radionuclides could form alteration products with the surrounding packing material and alter their sorptive behavior.

6. Summary of Additional Information Needed to Resolve the Issue by the Time of Construction Authorization Application

The following data will be needed to characterize the interaction behavior of the container with adjacent barriers:

- (a) A postulated container failure scenario which will permit an estimate to be made of the rate at which repository water passes through a perforated container to the waste form. This will enable the effect of water residence time on leachability to be determined.
- (b) Estimates of the thickness and thermal conductivity of oxide films on the container. This will permit temperature profiles through the waste package to be determined as a function of time.
- (c) An evaluation of the change in packing material performance as a result of interactions with corrosion products from the waste form and container.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

Several Work Elements in the SCR (W.1.6.A, W.1.7.A, W.1.12.A, W.1.19.B) generally cover the performance of waste package components after repository

closure. However, <sup>more</sup> more address in any detail the specific issues listed in section (6) above. It is possible that as the BWIP effort progresses, there <sup>these</sup> specific issues will require analysis and be factored into the ongoing research and development programs. To fully characterize <sup>these</sup> the changes in the physical and chemical <sup>nature</sup> name of changes in the container characteristics, however, an extensive effort is required since the changes will be severe as the residence time of the waste package in the repository becomes large. Thus, a satisfactory means of prediction these long term changes from <sup>short</sup> more- term experiments needs to be developed. <sup>term</sup>

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success

As specified in (7), above, the BWIP program does not directly address the long term physical and chemical changes in package components due to interaction effects. Because of the complexity of the problem, definite data may not only be obtained but it may be possible to make conservative estimates of the changes which can then be factored into waste package design. In doing so, the ability of the engineered system to <sup>meet</sup> ~~week~~ NRC performance criteria can be addressed.

Issue No. 2.6

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: What are the mechanical loads on the container vs. time? How do the packing materials alter the loading?
3. Importance of the Issue to Repository Performance

The basic importance of mechanical failure issues for BWIP containers is described in NRC Issue No. 2.4 and focuses on the container's role in radionuclide containment and source term quantification. The current Issue on the definition of the load vs. time relationship is of importance since it is needed to qualify the mechanical design of the container system, to estimate the degree of container breaching so that water flow rates around the waste form can be examined for leach rate analysis, and to estimate the time when the waste form will be contacted by water.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue:

§ 60.113 Performance of particular barriers after permanent closure

- (1) Engineered barrier system

- (i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

At this time the BWIP waste package design is tentative as are estimates of the anticipated temperature changes with time. Effective lithostatic/hydrostatic stresses also appear to be largely unknown. The recent work at Stripa (KBS-TR-22, 1977) shows that horizontal stresses in granite may be twice as large as those estimated from the rock overburden so that any mechanism failure of the container would more likely occur from this stress condition. Shear failure may also be a possibility due to rock movement along fault planes. At this time, therefore, significant uncertainties exist with respect to the identification of the stressing mode on the container, the magnitudes of the stresses, the effects on a deformable packing material in redistributing stresses, and the rate of deformation. Until these factors are quantified the mechanical failure time for a container cannot be determined.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

In order to successfully specify a mechanically-adequate container design the following additional data requirements will be required:

- (a) A conservative estimate of anticipated stress levels on the container system over the approximately 1000 year containment period.
- (b) A specification of the maximum compressive stresses (vertical and horizontal) and likely shear modes acting on the container system over the approximately 1000 year containment period.
- (c) Accurate estimates of the container temperature as a function of time.
- (d) A detailed description of waste package materials, geometries, and dimensions to determine stress-strain behavior under likely loading conditions.

- (e) Comprehensive information of creep and other mechanical properties for low carbon steel base and welded material for temperatures between 80-300°C. Effects of hydrogen level on deformation behavior also need to be determined.
- (f) Multicomponent stress analysis to determine how the waste form and packing material modify the loading and deformation of the container.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

The general outline in SCR Work Element No. W.1.2.A covers the recommended work scope in their Site Issue Analysis. It covers the proposed determination of temperature, loading and environmental histories for the waste package. However, close evaluation of the plan for Work Element W.1.2.A. on page 15.3-13 seem to focus only on chemical/hydraulic effects with little consideration for evaluating the loading to be expected on a waste package as a function of time. It seems that much more emphasis needs to be placed on the latter since <sup>mechanical</sup> week        failure modes may be extremely important with <sup>regret</sup> to demonstrating compliance with NRC performance objectives.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

Based on the discussion in (7) above it seems that extra emphasis will be needed on characterizing the waste package loading <sup>factor</sup>        for the anticipated BWIP repository design. Apart <sup>from their</sup> the overall BWIP <sup>text</sup>        plan which correlates environment and thermal conditions with loading <sup>factor</sup>        appears to be appropriate. A reevaluation of the text program should be carried out by NRC as full details of the loading are specified.

References:

1. KBS-TR-22, "The Influence of Rock Movement on the Stress/Strain Situation in Tunnels or Bore Holes with Radioactive Canisters Embedded in a Bentonite/Quartz Buffer Mass," 1977.

Issue No. 2.7

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: What are the possible corrosion failure modes for the container?
3. Importance of the Issue to Repository Performance

The container is generally considered to be the most important engineered barrier with respect to containing radionuclides. Because of this a container which remains unbreached by corrosion failure modes for extended periods will allow in situ radionuclide decay, and delay the onset of waste-form leaching. Thus, a container will be significant importance with respect to defining the radionuclide source term.

4. Portions of 10 CFR 60 that are Directly Connected to the Issue

§ 60.113 Performance of particular barriers after permanent closure

(a) General provision.

(1) Engineered barrier system.

(i) The engineered barrier system shall be design so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long time.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

Voluminous data exist on the corrosion of low carbon steel in a wide range of aqueous solutions. Uniform corrosion, pitting, crevice corrosion, stress corrosion cracking and hydrogen embrittlement are known to occur.

Although uniform corrosion rates in "clean" water are unlikely to cause failure of the BWIP container, based on available data on the range of uniform corrosion rates, pitting may present a problem since the rate of penetration may be higher by a factor of 4 to 11 (Southwell, Romanoff). Thus pits may penetrate the BWIP container during the containment period.

Crevice corrosion may readily occur in low carbon steel due to the formation of an oxygen concentration cell consisting of a small oxygen starved ~~anode~~<sup>anode</sup> and a large cathode with a higher surrounding oxygen level. In the crevice region (the ~~anode~~<sup>anode</sup>) the lack of oxygen allows the hydrogen ion concentration to rise and attract ions such as  $Cl^-$  to migrate to the crevice to maintain electroneutrality. As  $H_2$  builds up the metal in the crevice region is rapidly attached. A similar mechanism applies to pitting.

Carbon steel can suffer failure by stress corrosion cracking (SCC) under caustic environments and mechanical tensile stresses. Current theory uses a variety of mechanisms to describe all the characteristics and mode of SCC. These can be segregated into roughly three categories: cracks which are associated with either

(a) pre-existing active paths

(b) strain generated active paths

or (c) specific adsorption at subcritical stress sites.

Pre-existing active paths in an alloy are formed by microsegregation and precipitation within a metal, usually at grain boundaries. Local galvanic cells

are established weakening the metal against mechanical failure.

Microsegregation can be minimized by proper melting practice and careful consideration of casting technique. Precipitation can be minimized by keeping alloy content low and removing sulfur. (Parkins)

Strain generated active paths usually initiate at slip steps occurring at the surface of the metal. SCC proceeds intergranularly. Specific absorption paths require absorption of gases (particularly  $H_2$ ) into small cracks on the surface of the metal. (Parkins)

The role of hydrogen in SCC is not explicitly defined, although it is clear the  $H_2$  of  $m_4$  embrittlement will render a metal susceptible to SCC. (Logan and Yolken) In some cases if metal is in a strain condition, hydrogen will reduce the metal's yield strength to the point where it can fail mechanically. (Bhat)

The rate of hydrogen diffusion into a metal and the depth of attack (decarburization and fissuring) varies with metal heat treatment,  $H_2$  pressure, atmospheric moisture content and temperature. (Bhat, Gutzeit, Logan *et al.*) There exists an incubation period for attack, although it is shortened considerably by water vapor. Water vapor also increases the depth of hydrogen attack. However, Gutzeit and Thygeson report attack depths which logarithmically approach only a few millimeters. (Gutzeit and Thygeson Jr.)

Solution chemistry and mechanical strength also plays a dominant role in the modes of SCC. In aqueous chloride environments, for example, SCC is dependent on the yield strength of the alloy. Probability of failure increases for steels with strengths greater than  $689 \text{ MN/m}^2$  (100,000 psi), while steels less strong appear uniformly resistant. Cracking rate increases with temperature and  $Cl^-$  concentration, but the critical stress factor ( $K_{ISCI}$ ) does not.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

The following basic data will be needed to fully quantify the corrosion behavior of a low carbon steel container in BWIP:

- (a) A specification of the temperature-time history and load-time of the container.
- (b) A specification of the Eh, pH in the vicinity of the container as a function of time.
- (c) A determination of the water chemistry between the container and packing material.
- (d) Long term data on the uniform, pitting, and crevice corrosion rates for base and welded material.
- (e) Examination of the stress on the container and its effects on stress corrosion and hydrogen embrittlement.
- (f) Determination of gamma radiolysis effects in terms of oxygen and hydrogen pickup, and how these factors influence uniform and local corrosion.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods and Investigations to Provide the Information Needs of (6)

The SCR addresses the need to fully characterize corrosion failure modes in low carbon steel in order to determine whether the container can meet NRC radionuclide containment requirements. In the text program given in Work Element W.1.6.A (Table 15-2) the basic research will be centered on <sup>testing</sup> terrain of a range of candidate <sup>metals</sup> <sup>when a</sup> <sup>resistant</sup> <sup>v</sup> to determine the most corrosion reactions. Advance <sup>two to make</sup> <sup>metals</sup> <sup>priority</sup> texts will then be conducted on 2-3 high priority <sup>metals</sup> <sup>priority</sup> memos to be tested in the presence of packing material for a range of anticipated repository conditions, including <sup>radioactive</sup> radioaction. Uniform corrosion, <sup>uniform</sup> pitting, <sup>stress-</sup> stress-corrosion cracking, intergranular corrosion, crevice corrosion, and hydrogen embrittlement are all to be addressed.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success

The text program as briefly outlined in Table 15-2 is logical and complete. The program should be adequate if the text take into detailed confidence the localized conditions which will be present however the container and packing material. Also, alteration number be focussed on the effects of local inter\_\_\_\_\_ and precipitation which are known to significantly affect corrosion. Characterization of welds is also mandatory.

References

1. Southwell, C. R. and A. L. Alexander, "Corrosion of Metals in Aqueous Environments Over Extended Periods" in Proc. of the 3rd Internal Corrosion Conference, April 1969, pp. 19A. 1-15.
2. Romanoff, M., Underground Corrosion, NBS Circular 579, April 1957.
3. Parkins, R. N., "Stress Corrosion Cracking of Low-Strength Ferritic Steels," The Theory of Stress Corrosion in Alloys, 1971, NATO, Brussels.
4. Logan, H. L. and H. T. Yolken, "The Role of Hydrogen in the Stress Corrosion of Low Carbon Steels." 2nd International Congress on Metallic Corrosion, March 11-15, 1963, p. 109-115.
5. Bhat, U. V., "Diffusion of H<sub>2</sub> in Steel," Indian Institute of Metals - Transactions, 195?, Vol. ?, No. ?, p. 270-289.
6. Gutzeit, I. and I. R. Thyngson Jr., "Effect of Moisture on Decarbonization and Fissuring of Steel by Hydrogen and Elevated Temperatures and Pressures," Corrosion, 1967, Vol. 23, No. 10, p. 318-325.
7. Logan, H. L. and H. T. Yolken, "The Role of Hydrogen in the Stress Corrosion of Low Carbon Steels," 2nd International Congress on Metallic Corrosion, March 11-15, 1963, p. 109-115.

ISSUE NO. 2.8

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What is the effect of packing materials on the corrosion mechanisms for the container?
3. Importance of the Issue to Repository Performance:

The container's ability to restrict water ingress to the waste form surface depends on its resistance to corrosion failure. Any adverse interaction with packing materials is likely to accelerate uniform and localized corrosion and lead to a reduction in containment time.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue:

§60.113 Performance of particular barriers after permanent closure.

(1) Engineered barrier system

- (i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times.

5. Summary of the Present State of Knowledge, With Analysis of Uncertainties:

Most research carried out to date on metallic corrosion of container materials involves the exposure of metal samples in prototypic groundwater, i.e., single component testing. The presence of packing material adjacent to the container is likely to adversely affect the rate of corrosion by

providing a geometry equivalent to that for crevice corrosion in which local water chemistries may be dramatically altered. In the small volume of water between the container and packing material it is well documented that rapid decreases in groundwater pH values will occur, possibly leading to accelerated uniform corrosion and pitting and also hydrogen absorption. Complex corrosion produce/packing material interactions may occur which again may lead to a poorly defined local repository water chemistry. Radiolysis effects would also be magnified in the restricted volumes of water.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

Comprehensive data are needed to characterize container/packing material interactions in order to:

- (a) Determine Eh, pH conditions at the container surface and correlate these with long term local and uniform corrosion rates.
- (b) Determine chemical changes in the groundwater as a result of corrosion and radiolysis products and correlate these with local and uniform corrosion rates.
- (c) Determination of chemical changes in the groundwater as a result of its passage through packing materials and correlate these with local and uniform corrosion rates.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

The text programs described in Table 15-2 <sup>of the</sup> ~~of the~~ SCR, <sup>via.</sup> ~~fig.~~ Screening and advanced tests on container components with and without <sup>packing</sup> ~~policy~~ being presnet (Work Element W-1.6.A), <sup>directly</sup> ~~desirely~~ <sup>advances</sup> the need to determine the possible <sup>deterioration</sup> ~~deletion~~ effects of packing materials on corrosion failure rates. Total Eh and pH corrossions are a part of this text effort as well as radioaction effects.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of  
of Success:

The general <sup>mission</sup> on-line of the interaction texts specified in Table 15-2 appear satisfactory but the completeness and likely needs of the program will depend on the specific types of texts carried out, and the means by which extrapolation of text data to long term behavior <sup>prediction</sup> is developed.

References:

Issue No. 2.9

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: How do Eh, pH, and  $PO_2$  change with time in the vicinity of the container packaging?
3. Importance of the Issue to Repository Performance

Eh, pH, and dissolved oxygen content  $PO_2$  of the repository water will largely determine the containment life and the radionuclide release rate of the waste package. The corrosion rate of the mild steel container is expected to depend greatly on dissolved oxygen content (RHO-BWI-ST-15, 1982). The stability of the packaging material under hydrothermal conditions may depend upon the pH because the solubilities of component phases are affected by strongly alkaline or acid solutions (BNL-NUREG-31770, 1982). These parameters (Eh, pH, and controlled oxygen content of the repository water) will change with time following repository closure as the repository temperature changes and as transport processes and controlling chemical reactions proceed. Therefore, the values of Eh, pH, and  $PO_2$  within the waste package as a function of time must be known. These values are needed to determine whether laboratory tests can reflect waste package behavior in the changing repository environment.

4. Positions of 10 CFR 60 that are Directly Connected to the Issue

§60.113 Performance of particular barrier after permanent closure

(a) General provisions

(1) Engineered barrier system

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides

from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs. (ii) In satisfying preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that: (A) Containment of HLW within the HLW waste package will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission. (b) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be presented at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

##### 5. Summary of the Present State of Knowledge with Analysis of Uncertainties

Anticipated Eh, pH, and dissolved oxygen contents are presently derived from studies on basalt-seawater systems, direct laboratory measurements on synthetic groundwater contacted with crushed basalt and measurements on actual samples of basaltic groundwater (PNL-4382, 1982). These data imply that the repository Eh and pH will be controlled by the geochemical properties of the basalt. Strongly reducing anoxic conditions (Eh  $\sim$ -0.5 eV) are predicted to prevail over most of the repository lifetime. Oxygen introduced during repository emplacement operations is expected to be scavenged following repository closure. pH values  $\sim$ 6.0 to 9.6 are anticipated (RHO-BWI-ST-7, 1980). Uncertainties associated with Eh and pH predictions include the following: (1) the Eh of repository groundwater is difficult to measure under field conditions (PNL-4382-and NUREG/CR-2780). Present Eh data on field samples are largely

inferred from thermodynamic considerations or observed chemical specifications in redox couples, (2) the present data base on  $O_2$  scavenging kinetics in basalt-water systems is limited. Detailed information is not available on surface area and/or surface alteration effects which may limit uptake rates. Initially, it was estimated that several hundred years might be required to achieve equilibrium redox conditions following repository closure (RHO-BWI-ST-7). Recently, these estimates have been substantially reduced. (3) It is not yet clear how well "bulk" Eh and pH determinations carried out at high water to rock ratios reflect local conditions at the interface between packing and a (possibly corroding) container. (4) Recent experiments to investigate the geochemical reactions between groundwater and packing components are largely carried out under accelerated conditions in a static environment. Additional information is needed to relate accelerated hydrothermal test results to anticipated reactions and reaction rates in the repository environment.

6. Summary of the Additional Information Needed to Resolve the Issue by the Time of Construction Authorization Application

The reaction kinetics of oxygen scavenging should be determined and confirmed under actual field conditions over a range of temperature and groundwater flow. Rate limitations imposed by surface area and/or surface alteration of the basalt should be clearly defined. Analytical techniques used to predict "steady state" Eh conditions should be confirmed. The degree of correspondence between "bulk" solution properties and those local properties very near the packing-container interface should be established. This should include consideration of solution radiolysis effects (see Issue<sup>NC</sup> 2.10). It should be confirmed that the dominant reactions in accelerated hydrothermal tests will also be rate controlling in the repository environment over a range of flow rates and temperatures.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

TBD

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success

TBD

References:

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2. BNL-NUREG-31770, "Chemical Failure Modes of Bentonite and Zeolites in Discrete Backfill for Nuclear Waste Repositories," D. Eastwood, Brookhaven National Laboratory, August 1982.
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4. RHO-BWI-ST-7, "Engineered Barrier Development for a Nuclear Waste Repository in Basalt: an Intergration of Current Knowledge," M. J. Smith, Rockwell Hanford Operations, May 1980.
5. NUREG/CR-2780, Part 1, BNL-NUREG-51548, "Near-Field Repository Conditions in Basalt and Salt," B. Siskind and D. Hsieh, Brookhaven National Laboratory, May 1982.

Issue No. 2.10

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What is the radiolytic generation of hydrogen, oxygen and other species due to gamma radiation in the vicinity of the container.
3. Importance of the Issue to Repository Performance

The chemical durability of the barrier components which retard the progress of water to the waste forms depends sensitively upon the Eh, pH and oxygen content of the water to which these components are exposed. These properties in turn may be affected by gamma radiolysis processes in the groundwater. For example, corrosion rates of the mild steel container could be increased if radiolytic oxidants are generated in sufficient quantity. This issue is directly related to issue No. 2.9 which generally addresses the evolution of Eh, pH and  $PO_2$  in the vicinity of the container and packaging.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

60.113 Performance of particular barrier after permanent closure

(a) General provisions

(1) Engineered barriersystems

- (i) The engineered barrier system shall be designed so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered

barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

- (A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.
- (B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

A lot of information exists on radiolysis effects in pure water. Radiolysis data on rock salt brines is presently available and additional data are being generated. Radiation corrosion data are also available for various reactor applications and are being generated for container/brine systems.

These data have been recently reviewed (Glass, 1981) from the viewpoint of corrosion effects on HLW containers. However, a bounding analysis for conditions relevant to a basalt repository have not been carried out.

Uncertainties in the yields of radiolysis products in basaltic groundwaters under BWIP conditions largely reflect the lack of direct experimental data. As a first approximation one might consider basaltic groundwater as similar to deionized water. However, scavenging or recombination processes peculiar to the particular chemical makeup (including possible corrosion products, etc.) of the system under study might significantly affect this correspondence. It has been postulated (Smith, 1980) that under the strongly reducing conditions anticipated under steady state conditions in the backfill, water radiolysis would be suppressed by recombination process involving dissolved hydrogen. (calculations by Bullen and Modre, 1976) For water radiolysis in a reactor environment indicate that the concentration of radiolytically produced oxidizing species such as OH and  $O_2$  may be substantially reduced by dissolved hydrogen pressures of  $\sim 0.01$  MPa. On the other hand, when scavengers are present, water radiolysis can proceed far beyond this point. Irradiated basins, for example, may yield  $H_2$  pressures greater than 0.6 MPa. The major uncertainties, then in the radiolysis product yields and levels in the vicinity of the canister are associated with (1) the rates at which radiolytic process compete with the geochemical buffering process (2) uptake and loss measurements for dissolved hydrogen (3) the effects of possible \_\_\_\_\_ and (4) the rate at which oxidizing species are assumed in corrosion.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

Information to bound the formation rates (G-values) and steady-state concentration of  $O_2$ ,  $H_2$  and  $H_2O_2$  will be required. Other radiolysis products which might alter Eh or pH should be identified and their effects bounded. This information should consider the influence of radiation dose rates, temperature

and local conditions at the container packing interface. In particular, the following information should be obtained.

. The effect of dissolved hydrogen concentration on steady state concentration of radiolysis products,

. The rate at which dissolved hydrogen concentrations will \_\_\_\_\_ near the container/backfill interface due to geochemical reactions and transport processes.

. Identification of any \_\_\_\_\_ mechanisms, including corrosion which would compete with recombination processes for oxidation of radiolytic oxidants.

. The possible effects of local inhomogeneities (i.e., cells crevices, etc.) at the container-backfill interface.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

For an \_\_\_\_\_ container, only the corrosion tests under gamma irradiation described in work element W.1.3.A appear to be immediately \_\_\_\_\_. Backfill is to be exposed to external gamma irradiation in work elements W.1.3.A. It is not clear if the conditions of backfill experiments will be applicable toward desirring radiolysis effects at the container-backfill interface. These experiments appear to be the scoping type: In the corrosion experiments, hydrothermal tests are to be carried out to determine if radiation affects \_\_\_\_\_ rates. If an effect is observed, further measurements will be carried out. Detailed experimental conditions are not stipulated.

Hydrothermal testing experiments will radioactive waste forms as a radiation source and also describe in work element W.1.3.A. In principle, these should display radiation effects within the entire waste package, in the presence of interacting components. It may be difficult, in such a complex system, to extract data on particular radiation effects (i.e., suppression of radiolysis

by dissolved hydrogen) from these experiments. The extent of interactive between these experiments, and the backfill and corrosion these under external irradiation was not described.

8. Analysis of (7) As To Completeness, Practicality and The Likelihood of Success

The experiments described in the planned approach do not, in general, appear capable of generating detailed information on the anticipated concentration of radiolysis process. This is admittedly judgemental, since the plans are not set forth in detail. However, no specific mention is made or directly identifying radiolytic species or determining the kinetic aspects of the radiolysis mechanism (dose rate effects, gaseous and steady state concentration, etc.) Rather the approach is to determine now (if at all) radiation affects a particular process (e.g. corrosion) under a particular set of conditions (e.g. hydrothermal contact with reducing groundwater at low pH). Subsequent plans will depend on the results of these scoping experiments.

In the absence of a mechanistic study on radiolysis effects themselves a major concern with the present approach is how well the planned experiments reflect worst case or bounding conditions. This topic is not discussed in the test plans; indeed, some mechanistic consideration might be necessary to define such conditions. For example, if a locally reducing environment and/or a high hydrogen fugacity is postulated to be important radiolysis effects, then scoping tests should reflect the manner and extent to which such conditions may be established in the repository environment. Tests where the geochemical reactions are accelerated or the hydrogen partially contained may mask the significance of radiolysis may be masked.

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Issue No. 2.11

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What is the dependence of the oxygen removal rate from packing material upon temperature, pressure, radiolysis, packing materials physical characteristics, groundwater flow rates, composition, and time?
3. Importance of the Issue to Repository Performance

The time evolution of Eh values within the waste package following repository closure is said to be dominated by oxygen scavenging in the packing material following resaturation. Eh is a key factor in the performance of the packing, container, and waste form. The rate at which this oxygen scavenging occurs is broadly relevant to all issues concerning the geochemical environment of the packing, container, and waste form (see issues 2.9, 2.10 and 2.18). The ability of the packing material to provide a low Eh environment must be known over a range of external variables, both to establish anticipated behavior and to determine operating limits for waste package performance.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

§ 60.113 Performance of particular barriers after permanent closure

(a) General provision.

(1) Engineered barrier system.

(i) The engineered barrier system shall be design so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process

which results in small fractuinal releases to the geologic setting over long time. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.135 Criteria for the waste package and its components.

(a) High-level-Waste package design in general.

(1) Packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.

(2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

1. Information on the fundamental rate constants which describe the oxygen scavenging reaction(s), in the vapor and liquid phases. This should describe the effects of external variables such as temperature, pH, and pressure.
2. Information on the effect of "process parameters," such as water-to-rock ratio, surface to volume ratio, repository flow rate and radiolysis effects (see Issue 2.10) on the extent to which the scavenging reactions operate. In particular, it should be established how oxygen scavenging rates will be affected as reaction products accumulate on material surfaces.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

TBD

8. Analysis of (7) As To Completeness, Practicality and The Likelihood of Success

TBD

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1. RHO-BWI-ST-7, "Engineered Barrier Development for a Nuclear Waste Repository in Basalt: an Integration of Current Knowledge," M. J. Smith, Rockwell Hanford Operations, May 1980.
2. Wood, M. I., "Experimental Investigation of Sodium Bentonite Stability in Hanford Basalt," Rockwell Hanford Operations, Paper D 11.8, Symposium D., Materials Research Society Annual Meeting, Boston, Massachusetts, November 1982 (in press).

Issue No. 2.12

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: How do microbes effect conditions affecting corrosion modes? What effect do microbes have on the conditions affecting transport?
3. Importance of the Issue to Repository Performance

Corrosion of the container is expected to be a critical consideration in determining how water will penetrate the waste package. It has been recognized for some time (cf. Shrier, 1976) that the corrosion rates of metals, and in particular, iron, can be affected or enhanced by microbial activity under certain conditions. Microbial activity may also affect pH and redox environments; if these effects were to occur under repository conditions radionuclide transport properties in the backfill could be modified. This would affect the manner in which radionuclides are released from the waste package.

Microbial activity in a deep geologic repository has not been extensively studied. Under anticipated repository conditions, one might anticipate that microbial effects would be relatively limited. A bounding analysis, however, is necessary to establish the extent and significance of microbial effects on conditions within the waste package.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

§ 60.113 Performance of particular barriers after permanent closure.

(a) General provisions.

(1) Engineered barrier system.

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (b) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional release to the geologic setting over long times. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release of any radionuclide from the engineered barrier system follows the containment period shall not exceed one part in 100,000 per year of the inventory of the radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.135 Criteria for the waste package and its components.

(a) High-level-waste package design in general.

(1) Packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.

(2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge, With Analysis of Uncertainties

Microbial effects on corrosion have been studied for some time in connection with behavior of pipes, and other objects, buried in soils. Corrosion may be enhanced either through this action of microbial metabolic products, such as sulfuric acid or sulfides, cathodic depolarization associated with anaerobic growth, or local changes in solution chemistry which establish electrochemical cell (Shrier, 1976). It has been estimated that bacterial activity may account for as much as 50% of the failures of stainless steel buried in soils. Perhaps the most important effects in this respect are associated with the actions of bacteria on sulfur-containing compound. Under aerobic conditions, *Thiobacillus thio-oxidans* may produce sulfuric acid by direct oxidation of sulfur; *Ferrobacillus* (or *Thiobacillus*) *ferro-oxidans* may oxidize the ferrous ions in  $\text{FeS}_2$  producing acid waters. It is noteworthy that the *Thiobacillus* attacks the iron directly. (Alexander, 1977). Other sulfate reducing species such as *Desulfurivibrio* *Resulfuricans* may produce corrosions of iron under anaerobic conditions both by generating the corrosive species  $\text{H}_2\text{S}$ , and possibly by a

mechanism involving <sup>entire</sup> control dedi\_\_\_. Acid species produced will of course vary the local pH; Eh values will also be affected by microbial redox behavior. Anaerobic microbes, for example may reduce the Eh value of a soil from 0.4 to - 0.1 v within one month after flooding (Spencer, et al., 1963).

In the present context, the major uncertainty in assessing microbial effects lies in estimating the effect of repository conditions on microbial activity. The waste package represents a hostile environment for microbes - temperatures in excess of 100°C coupled with a relatively intense ionizing radiation field would appear to provide an initially sterile atmosphere, although this point must be established. It seems most plausible that microbial activity in the waste package could begin if microbes are transported to its vicinity somewhere near the end of the thermal period-several hundred years after closure. It remains to be established if this is a viable scenario, and how well the available nutrients (in particular carbon) would support an anaerobic microbe population. Microbial activity has proved troublesome in gold and coal mining operations. On the other hand, Belgian workers (Dresselaers, 1982) examining long term (60-90 years) corrosion of cast iron structures in underground coal mines were unable to find any evidence of Thiobacillus, ferro-oxidans, or Desulfurivibrio Desulfuridans. Possibly, some preventative measures were taken. In any event, it is difficult to generalize about microbial activity, and site-specific evaluations are needed.

ISSUE NO. 2.13

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What is the solubility of radionuclides vs. time in the vicinity of the waste form and packing materials? How are the radionuclides released from the waste form?
3. Importance of the Issue to Repository Performance:

Radionuclides released into a volume of water adjacent to the waste form will be partitioned between aqueous species, radiocolloids and pseudocolloids. The concentrations of each of the components at any time is related to the physico-chemical environment and degradation modes of the waste form. The mass flux of radionuclides from the waste package to the near field environment can be no larger than the product of the radionuclide concentration (including aqueous species and other forms) times the volumetric flux of water through the waste package. The relationship of radionuclide solubilities and waste form degradation modes to time dependent parameters such as temperature, redox potential and pH must be known before the release rate of radionuclides from the waste package can be predicted.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue:

§ 60.113 Performance of particular barriers after permanent closure

(a) General provisions

(1) Engineered barrier system

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events (A) containment of HLW will be

substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

- (A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.
- (B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.135 Criteria for the waste package and its components.

(a) High-level-waste package design in general

- (1) Packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility of the geologic setting.
- (2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties:

The solubilities of radionuclides and the durability of waste forms over a wide range of physico-chemical conditions must be understood in order to predict radionuclide release rates during the regulatory period. As discussed in Issues No. 2.3 and 2.9 during the containment period, the immediate surroundings of the waste form may change from a high temperature, acidic, oxidizing environment to a cooler, alkaline, reducing one. The properties of a glass waste form may change due to devitrification and radiation damage (Issue No. 2.14).

At present it is not possible to predict the solubilities of radionuclides at elevated temperatures (200-300°C) with any confidence. Most of the available radionuclide stability complexation constants have been obtained at temperatures below 50°C (Apps, J.A.). Experimental determinations of solubilities of waste form components at higher temperatures have shown that it is difficult to assign solubilities to waste elements at the present time (Fullam, H. T.). It is not possible to determine the temperature dependence of radionuclide solubilities without a large number of solubility measurements at several temperatures (Apps, J. A.). Based on a limited amount of data, it has been

suggested that some of actinides and rare earths in the waste form may exhibit a negative temperature coefficient of solubility (Ogard, A.).

Waste elements which can have several oxidation states may exhibit Eh-dependent solubilities. Experimental studies at low temperatures (25°C) suggest that the solubilities of uranium, neptunium, technetium and selenium under oxidizing conditions are several orders of magnitude higher than they are under reducing conditions (Wood, B. J.). Other multivalent elements such as plutonium and americium have solubilities which are insensitive over the Eh range relevant to waste repositories (Wood, B. J.). The solubilities of monovalent waste elements may be independent of Eh; however, if the element forms complexes with ligands whose concentration are Eh-dependent (e.g.,  $\text{SO}_4^{2-}/\text{HS}^-$ ), then the solubility may depend on the redox potential.

The solubilities of elements which form aqueous hydroxyl complexes or solid oxides and hydroxides (e.g.,  $\text{Sb}(\text{OH})_3^0$ ,  $\text{Sn}(\text{OH})_4^0$ ,  $\text{U}(\text{OH})_5^-$ ,  $\text{UO}_2(\text{OH})_2$ ,  $\text{Pu}(\text{OH})_4(\text{am})$ ,  $\text{Am}(\text{OH})_2^+$ , may exhibit a complicated dependence upon solution pH (Apps, J. A.).

The leaching behavior of glass is similarly dependent upon a large number of environmental characteristics. These include temperature, Eh, pH, radiation damage (Burns, W. G.), thermal history (Clark, D. E.), and solution composition (Lanza, F.). All of these parameters will vary during the regulatory period. The deposition of a surface film of insoluble oxides and hydroxides or the formation of a leached layer will reduce the leach rate. Leachability generally increases at higher temperatures and can be related to the Arrhenius equation (Westsik, 1981). The actual temperature relationship, however is, element specific and depends upon the solution chemistry and occurrence of secondary hydrothermal reactions (Westsik, 1980; Stone, J.). Spent fuel leaching is less dependent on temperature and may show a negative temperature dependence (McVay, G. L.).

In an open system, where waste elements are flushed from the waste package by rapidly flowing groundwater, the leach rate will determine the radionuclide release rate. Under stagnant conditions, where the products of leaching accumulate in the leachant, radionuclide solubilities will control the release rate.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

As discussed in the previous paragraph, radionuclide complexation data must be obtained for the most toxic elements at several elevated temperatures. The data must be obtained under the redox conditions that are most likely to prevail at these temperatures. Leaching studies should be performed under similar conditions and should be carried out with "aged" devitrified glasses as well as fresh samples. The stability of the leached layers that forms during glass dissolution should be evaluated.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

(TBD)

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

(TBD)

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Issue No. 2.14

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: What properties of the waste form change with time and alter the ability of the waste form to contribute to the overall performance of the repository system or impact on the performance of other barrier materials and properties of the site.
3. Importance of the Issue to Repository Performance

The solidified waste form is the source term for release of radionuclides to the rest of the repository system and subsequently to the biosphere.

4. Portions of 10 CFR 60 that are Directly Connected to the Issue

§ 60.113 Performance of particular barriers after permanent closure

(a) General provisions.

(1) Engineered barrier system.

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional release to the geologic setting over long times. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

- (A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.
- (B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in the uncertainties in assessing repository performance are large, special emphasis is placed upon the ability to contain to wastes by waste packages within an engineered barrier system. This is known as the containment period. The engineered barrier system includes the waste packages and the underground facility. A waste package is composed of the waste form and any containers, shielding, packing, and absorbent materials immediately surrounding an individual waste container. The underground facility means the underground structure, including openings and backfill materials, but excluding, shafts, boreholes, and their seals.

Following the containment period special emphasis is placed upon the ability to achieve isolation of the wastes by virtue of the characteristics of the geologic repository. The engineered barrier system works to control the release of radioactive material to the geologic setting and the geologic setting works to control the release of radioactive material to the accessible environment. Isolation means the act of inhibiting the transport of radioactive material to the accessible environment in amounts and concentrations within limits.

##### 5. Summary of the Present State of Knowledge with Analysis of Uncertainties

Properties of the waste form will impact on the underground facility, particularly the groundwater. Vitrified radioactive waste and spent fuel will cause both thermal and radiation induced changes in the groundwater. Since the backfill performance, the corrosion behavior of the container(s) and the

leaching of the waste form itself are all dependent on the water pH, Eh, and chemical composition, the changes in these properties induced by the presence of the waste should be addressed. (It should be noted that by simply increasing the temperature of the medium, leaching can be increased orders of magnitude and corrosion rates will also be enhanced.) The effects of the water environment will alter the time of containment and the rate of radionuclide release.

In addition, the waste form may undergo changes with time that affect the rate at which radionuclides are released. Devitrification (Hench, 1982) phase separation as well as changes in the glass induced by fission product decay may alter the leach properties of the glass. Recently it has been suggested that the phase separation resulting from isothermal devitrification of the glass may result in as much as a factor of 140 increase in the leach rates of glass. Decay of the fission products will produce compositional changes in the glass, the magnitude of which will depend on waste composition.

There is also evidence that (Wicks, 1982) surface film formation on SRP glass results in a more durable waste form. The film which is rich in Fe and Mn appears to be protective. In contrast, the presence of iron in the leaching medium (McVay, 1982) has been shown to increase the leach rate of glass. While these results are not directly comparable, the question of surface film formation and the effect of the environment and other package components on the durability of film is an issue that should be addressed if film formation is claimed to enhance the performance of the glass. For spent fuel the effects of aging on its performance have not been determined, nor have the effects of cladding failure and corrosion product buildup.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

The long term performance of the repository system is affected by the thermal and radiolytic changes in the groundwater caused by the presence of the waste. In addition, the performance of man made barriers and the rate of release of

radionuclides from the waste form is affected by the environment. The following information is necessary to close out these issues:

- a. Combined thermal and radiolytic effects on groundwater.
  - b. Engineering studies of the variation in leach rates alone and with other barrier materials in "typical waters" which include the effects of temperature and radiation.
  - c. Effect on leach rates/dissolution rates in "typical waters" as a result of changes in glass properties induced by fission product decay (aged glass), devitrification/phase separation. The impact of film formation and the effects of the environment (i.e., water composition, etc.) and other package components.
  - d. Effect on leaching from spent fuel in "typical waters" as a function of changes in the spent fuel in the presence of other barriers, and considering the effects of radiation and heat.
7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

The text (Chapter 11) specifically states that the present data base is inadequate for determining the performance of the waste form (either borosilicate glass or spent fuel) in basalt repository conditions. The problems of devitrification, phase separation, and compositional changes in glass as well as phase change and compositional variability in spent fuel are noted. The potential interaction of the waste form with other barrier materials as a function of temperature radiation and groundwater chemistry (including Eh and pH) are also discussed.

A program is planned to determine the performance of package materials under basalt conditions (W1.1A). The work scoped in this work element has complementary test activities to consider the aspects of radiation and barrier material interactions (W1.6A, 1.12A, and W3.7A). These tests appear to be planned for hydrothermal conditions only.

8. Analysis of (7) As To Completeness, Practicality and The Likelihood of Success

The description given in the work plans is inadequate to insure that the program is complete and likely to succeed in addressing 6(a)-(d). For example, the materials testing plan (W1.1A) appears to be designed to evaluate the performance of the waste form under hydrothermal conditions alone. This assumes that mechanisms of leaching will not change with time and would also infer the potential problems of long term changes in the waste form (phase separation compositional changes, etc.) are not to be addressed. If containment fails when hydrothermal conditions no longer apply and long term changes in the waste form have occurred, the leach rates or dissolution characteristics determined under hydrothermal conditions may have no similarity to the behavior at later times. Similarly, the programs designed to address the effects of radiation on waste form behavior do not appear to address lower temperatures taking into account the possibility of loss of containment when hydrothermal conditions no longer apply.

It is clear that leach rates under hydrothermal conditions will not satisfy the controlled release criterion. There is not enough information in the plan to estimate the means or effectiveness of extrapolating hydrothermal data to a lower temperature.

The programs to address barrier material interactions are again not described in enough detail to insure that 6(b)-(d) will be resolved.

## References

1. Hench, L., NRC Research Contractor Meeting, Silver Spring, Maryland, October 7-8, 1982.
2. Wicks, G. G., B. M. Robnett, W. D. Rankin, "Chemical Durability of Glass Containing SRP Waste - Leachability Characteristics, Protective Layer Formation and Repository System Interactions" presented at the Fifth International Symposium on the Scientific Basis for Radioactive Waste Management, Berlin, Germany, June 7-10, 1982.
3. McVay, G. L., "Review of Recent PNL Research Activities Related to Glass Leaching Mechanisms of Nuclear Waste Forms, May 19-21," PNL-4382, August 1982.

## Issue No. 2.15

1. Name of the Site: BWIP - Hanford, Washington

2. Statement of the Issue:

2.15 . What is the effect of water resident time on release of radionuclides from the waste form?

3. Importance of the Issue to Repository Performance

In modeling rates of release of the various components of solid nuclear waste forms exposed to chemical degradation in aqueous media, a distinction exists between the process which control the overall degradation rates and transport of material away from the waste form under conditions of short residence times on one hand and of (high flow) long residence times (low flow) on the other. At high rates (or high dilutions) the degradation rates are largely affected by the leaching kinetics of the solid in water, where the composition of the water reflects the conditions prevailing in the environment of the waste package rather than interaction with the waste form. At low flow rates the loss rates depend in part upon the thermodynamic solubility and upon the rate at which the water in contact with the solid (which has been considerably modified as a result of dissolution of species from the waste form) is replaced with fresh, unreacted water. Under repository conditions, water exchange rates are likely to be low in a large number of cases, and therefore solubilities constitutes a key factor in determining the long-term durability of the material.

As mentioned above, water subjected to prolonged interaction with the material becomes substantially altered. This alteration of the composition affects the reactivity of the medium with respect to the dissolution of a particular species from the waste form in the following ways: (i) pH changes, e.g., increase in pH due to dissolution of alkaline components from the solid, cause large

effects on solubility limits as well as on leach rates;  
 (ii) increasing concentration levels of species of interest may result in approaching saturation in the case of nearly insoluble species; (iii) increasing concentrations of other degradation products can affect subsequent dissolution of the species of interest due to secondary interactions; (iv) increasing solute concentrations in the aqueous phase can give rise to phenomena such as re-adsorption, ion-exchange and other modifications of the solid-liquid interface which affect further material transport processes across the surface (v) pH changes as discussed in (i) above may influence formation of complex ions for example, carbonate oxalate, sulfonate and ferro-silicate complexes, and colloidal particulates which in turn pick up radionuclides and effect their mobilization. Macedo, Avgado all of these processes affect transport of radionuclides in the engineered barrier system and hence rates at which they will be released from the system.

For an engineered system designed which does not include barriers which impede radionuclide transport or provide sorptive properties the release rate from the waste form would determine the engineered system performance. For engineered systems with multiple barriers controlling release the waste form release rates will greatly affect the reliability of the overall system performance.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue:

§60.113 Performance of particular barriers after permanent closure.

§60.135(a) Requirements from the waste package and its components; waste package design requirements for high level waste.

5. Summary of the Present State of Knowledge, With Analysis of Uncertainties:

General correlations of release rates of radionuclides from borosilicate glubs and spent fuel exist for many different conditions. Release are controlled by diffusion mechanisms for young glass and by dissolution of the glass over the long term. Typical values for dissolution rates range from  $10^{-4}$  g/cm<sup>2</sup>-day to  $10^{-7}$  g/cm<sup>2</sup>-day depending on water resident times and resulting solution chemistry, (BNL-NUREG-51494).

Knowledge of the solution (pH and dominant soluble and colloidal species) chemistry in the multicomponent system including, aged glass, canister corrosion products and packing material where water resident times is a variable, represents a major uncertainty in resolution of this issue.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

Multicomponent testing of materials utilized in the waste package with conditions controlled, i.e., gamma radiation, temperature and heat flux, must be accomplished to verify anticipatal ranges of the key chemical parameters, Eh and pH, are properly identified as a function of water resident time. Testing to identify complexes and colloifual partides which occur in the multicomponent system must aslo be accomplished.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods and Investigations to Provide the Information Needs of (6):

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

References:

1. Macedo, P.B., Etal.; "Aluminosilicate Saturates As A Solubility Control In Leaching of Nuclear Waste-Form Materials" PNL-4382, Workshop on the Leaching Mechanisms of Nuclear Waste Forms, May, 1982.
2. Avogadra, C.N., Etal.; "Underground Migration of Long-Lived Radionuclides Leached From A Boreosilicate Glass Matrix"; IAEA-SM-257/73, International Symposium on Migration in the Tesstrial Environment of Long-Lived Radionuclides From the Nuclear Field Cycle; July, 1981
3. BNL-NUREG-51494, Review of DOE Waste Package Program, Subtask 1.1, February, 1981.

Issue No. 2.16

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: What are the ranges of residence times of a unit volume of water in contact with a unit over waste form and when do the residence times occur? For spent fuel, how do hulls change the effective residence time?
3. Importance of the Issue to Repository Performance:

In modeling rates of release of the various components of solid nuclear waste forms exposed to chemical degradation in aqueous media, a distinction exists between the processes which control the overall degradation rates and transport of material away from the waste form under conditions of short residence times on one hand and of (high flow) long residence times (low flow) on the other. At high rates (or high dilutions) the degradation rates are largely affected by the leaching kinetics of the solid in water, where the composition of the water reflects the conditions prevailing in the environment of the water reflects the conditions prevailing in the environment of the waste package rather than interaction with the waste form. At low flow rates the loss rates depend in part upon the thermodynamic solubility and upon the rate at which the water in contact with the solid (which has been considerably modified as a result of dissolution of species from the waste form) is replaced with fresh, unreacted water. Under repository conditions, water exchange rates are likely to be low in a large number of cases, and therefore solubilities constitute a key factor in determining the long-term durability of the material. As mentioned above, water subjected to prolonged interaction with the material becomes substantially altered. This alteration of the composition affects the reactivity of the medium with respect to the

dissolution of a particular species from the waste form in the following ways:

- (i) pH changes, e.g., increases in pH due to dissolution of alkaline components from the solid, cause large effects on solubility limits as well as on leach rates;
- (ii) increasing concentration levels of species of interest may result in approaching saturation in the case of nearly insoluble species;
- (iii) increasing concentrations of other degradation products can affect subsequent dissolution of the species of interest due to secondary interactions;
- (iv) increasing solute concentrations in the aqueous phase can give rise to phenomena such as re-adsorption, ion-exchange and other modifications of the solid-liquid interface which affect further material transport processes across the surface
- (v) pH changes as discussed (i) above may influence formation, formation of complex ions for example, carbonate, oxidate, sulfonate and ferrisilute complexes, and colloidal particules which in turn pick up radionuclides and effect their mobilization (Macedo, Avogadro). All of these processes affect transport of radionuclides in the engineered barrier system and hence rates at which they will be released from the system.

4. Portions of 10 CFR 60 that are Directly Connected to the Issue

§ 60.113 Performance of particular barriers after permanent closure

(a) General provision.

(1) Engineered barrier system.

- (i) The engineered barrier system shall be design so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small

fractural releases to the geologic setting over long time. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

- (ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:
  - (A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.
  - (B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.135 Criteria for the waste package and its components

- (a) High-Level Waste package design in general
  - (1) Packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.
  - (2) The design shall include but not be limited to consideration of the following: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength,

mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

The residence times of water at the waste form are dependent upon the design of the engineered system and the thermal-hydraulic boundary conditions through time affecting flow in the system. Differential pressures in the engineered system and near field, including those created by temperature will act to drive water from one part of the system to another and to effect mixing within the system. Analytical models are generally available to evaluate systems whose hydraulic characteristics are dominated by diffusion mechanisms or by convection. Uncertainties in material properties, particularly hydraulic conductivity, and the diversions of connective flow paths, for example, cracks in packing materials, holes or fissures in containers and cracks within waste forms, throughout the life of the engineered system.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

Verification of the long term hydraulic conductivity of packing materials, for example, bentonite clay/crushed basalt aggregates, in changing repository conditions is of prime importance. Chemical alterations and changes in mechanical characteristics of the packing are key parameters which will effect hydraulic conductivity (Howard, Bolmgren ~~Garven~~). Knowledge of residence are the source of uncertainty in these evaluations to date. Knowledge of residence times for water in engineered barrier system has been based on bounding calculations using hydraulic conductivities for typical packing materials measured in field tests as well as laboratory test (Bolmgren).

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success

## References

1. Macedo, P. B., Etal.; "Aluminosilicate Saturates as a Soubility Control In Leaching of Nuclear Waste-Form Materials" PNL-4382, Workshop on the Leaching Mechanisms of Nuclear Waste Forms, May, 1982.
2. Avogadro, C. N., Etal.; "Underground Migration of Long-Lived Radionuclides Leached From A Boreosilicate Glass Matrix;" IAE-SM-257/73, International Symposium on Migration in the Tesstrial Environment of Long-Lived Radionuclides From the Nuclear Field Cycle; July, 1981.
3. Howard, J. D. and White, W. B., "Clay Metaporphism: A Natural Analog For Argillaceous Backfill Behavior," DOE/NTWS; November1, 1981.
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ISSUE NO. 2.17

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: How do the packing (spent fuel hulls if applicable), canister, and container materials and/or their alteration products interact with waste form to cause its alteration and/or effect release of radionuclides?
3. Importance of the Issue to Repository Performance:

Interaction of packing, canister and container materials and/or their alteration products and waste form can affect the mechanisms by which waste form release radionuclides and adversely reduce the overall containment capability of the repository. The time period and the rate at which this interaction take place must be known to evaluate the interaction's overall effect over the long term.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue:

§ 60.113 Performance of particular barriers after permanent closure

(a) General provisions

(1) Engineered barrier system

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small

fractional releases to the geologic setting over long times. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.135 Criteria for the waste package and its components

(a) High-Level Waste Packing Design in General

(1) Packages for HLW shall be designed so that the in-situ chemical, physical and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste

packages or the performance of the underground facility or the geologic setting.

- (2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties:

Little is known about synergistic effects of waste form leaching and corrosion of its containers. Sorption of metal ions onto glass surfaces are known to reduce the rate of aqueous corrosion of glass including beryllium and zinc (Hudson), calcium (Oka), aluminum (Iler, Dilmore) and lanthanides (Buckwalter and McVay). A recent study on different candidate container materials has provided the following observation (Buckwalter and Pederson): (a) glass leaching in lead container was reduced by more than two orders of magnitude from that measured in teflon, while leaching in aluminum containers was reduced by nearly one order and (b) relatively minor effects on glass leaching were measured in copper, tin, and titanium containers.

Chemisorption of metals on glass was reasoned to be the cause of this reduction in glass leach rate<sub>A</sub>. <sup>(Buckwalter and Pederson)</sup> Ferrous base metals have not been included in the reference ~~(6)~~ study.

Effects of iron on waste glass leaching was subsequently studied (McVay and Buckwalter). It was reported that the presence of <sup>c</sup>du<sub>A</sub>tile iron in deionized water, tuff, and basalt groundwaters containing PNL 76-68 borosilicate glass cause changes in the leaching characteristics of the glass. Formation of iron silicate precipitates effectively removed many elements from solution. As a result, the basalt and tuff groundwater behave<sub>A</sub><sup>d</sup> similar to deionized water. The precipitates also retard<sub>A</sub><sup>e</sup> saturation effects. Iron/glass interactions resulted in iron enhancing glass leaching and glass enhancing iron corrosion.

Clay-water has been found to leach glasses up to five times faster than distilled water (Van Iseghem). Although leach rates are found in general in the afore-mentioned studies to saturate after relatively short periods, transport of the products of leaching/corrosion can sustain leach/corrosion rates close to that by deionized water.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

Short of in-situ experiments, leaching experiments must account for synergistic effects between the packing, canister, backfill waste form and/or their alteration product in conditions simulating those in the repository environment. To account for long time periods, altered groundwater as well as simulated aged waste forms must be used to reduce the uncertainties of adverse interactions.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

(TBD)

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

(TBD)

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7. McVay, G. L. and C. Q. Buckwalter, "The Effect of Iron on Waste Glass Leaching," PNL-SA-10474, Pacific Northwest Laboratory, Richland, Washington, May 1982.
8. Van Iseghem, P., W. Timmermans and R. De Batist, "Interaction of Vitrified High-Level Waste with Clay Environment," International Seminar on Chemistry and Process Engineering for High-Level Liquid Waste Solidification (KFA Julich, June 1-5, 1981).

Issue No. 2.18

1. Name of the Site: Basalt Waste Isolation Project (BWIP), Hanford, Washington
2. Statement of the Issue: How does the Eh, pH, and  $AO_2$  change with time in the vicinity of the surface of the waste form?
3. Importance of the Issue to Repository Performance

The manner in which the waste form releases radionuclides (General Issue 4) and the manner in which radionuclides are released from the waste package (General Issue 5) will depend upon pH and redox conditions near the waste form. The dissolution or leaching behavior of the waste form will be sensitive to local pH and Eh conditions (see Issue 4.1). If, in fact, radionuclide transport within the waste package is controlled by solubility limitations, the evolution of Eh and pH within the waste package will be of particular importance since solubilities may depend strongly on redox conditions and pH. As pointed out under Issue 3-3:4:1, these parameters will change with time following repository closure as the repository temperature changes, and as transport processes and controlling chemical reactions proceed. The evolution of Eh, pH, and  $PO_2$  within the waste package will be known in order to determine if laboratory tests over a range of quasi-steady conditions can accurately reflect waste package behavior in the changing repository environment.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

§ 60.113 Performance of particular barrier after permanent closure

- (a) General provisions
- (1) Engineered barrier system

- (i) The engineered barrier system shall be...(fill in from Rule)
- (ii) In satisfying the preceding requirement...(fill in from Rule).

5. Summary of the Present State of Knowledge, With Analysis of Uncertainties

Information on the anticipated Eh, pH, and dissolved oxygen content within the waste package has been discussed in connection with Issue 3.3.4.1. To the extent that local conditions near the surface of the waste form are controlled by the crushed basalt backfill (Wood, 1982; RNO-BWI-ST-IS-1982) strongly amoxic conditions (Eh ~ -0.5 V) are expected to prevail for most of the repository lifetime. Ph values are expected to range from 9 to 6, again assuming that dissolution of silicic acid in the basalt is the rate-controlling process.

Several uncertainties in the determining of the anticipated evolution of Eh and pH within the waste package have been described under Issue 3.3.4.1. These include (1) a lack of kinetic data to determine the rate at which geochemical reactions in the basalt would change the pH and Eh following repository closure and (2) confirmation that local pH and Eh conditions at the waste form surface will in fact be continued by reactions associated with basalt.

Uncertainties involving the kinetic data on basalt-related reactions have been referred to under Issues 3.3.4.1 and 3.3.4.1.2. Uncertainties in establishing the dominant mechanisms controlling Eh and pH at the waste form interface have to do with the waste form/groundwater interaction and with radiolysis effects. It has been recognized for some time (cf) NUREG/CR-2333 BNL-NUREG-51458; PNL 4382a) that local chemical condition may be modified by dissolution of the waste form. A familiar example is the increase in pH when alkaline components are extracted from simulated waste scan in leaching experiments. This, however, may be offset by the presence of components such as phosphates, which buffer the leachate. [It is also worth noting that under certain conditions solubilities may be a strong function of pH.] Work in underway (PNL 4382b) in which the reaction between waste glass and basaltic groundwater is being studied under hydrothermal conditions in a static environment. Some data are available (RNO-BW-SA-194 P) on the effect of hydrothermal reactions

on the evolution of pH within the systems supercalcine + basalt + water and supercalcine + water. These experiments indicate that the pH values may be affected (substantially lowered) by the presence of fine particles in the coarsely powdered samples. Consequently, it is not yet clear how well experiments on powdered samples reflect conditions near the surface of actual waste forms, which may be more nearly monolithic and in close proximity to container surfaces. Recently, it has been reported (McVay, 1982) that the leaching kinetics of waste glass may be significantly influenced, if not dominated, by the presence of ductile iron in the system.

The effects of irradiation on pH and redox continues have been discussed in conjunction with Issues 3.3.4.1.1./5.1.4.1 and 5.2.1.2. Briefly, radiolysis may affect both pH and redox benuion (Strickert and Rai, 1982; Nash, et al. 1982), and leaching kinetics for waste glasses (cf, NUREG/CR-2333 Section 5.2.1.2). In general, ionizing radiation tends to increase leaching rates. Depending upon experimental conditions the increase may be substantial on rather modest. Some, but not all, of this affect can apparently be attributed to a pH decrease due to the elimination of nitric acid by the radiolysis oxidation of  $N_2$  in the presence of water. Presumably, this effect could also operate in the repository, utilizing atmospheric nitrogen introduced during the operating period.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

The significance of waste form - groundwater reactions in determine local pH and Eh conditions should be established for waste forms of interest. In order to provide a basis for extrapolating laboratory results to repository behavior, the degree of acceleration in laboratory experiments should be established. In particular, the kinetics of rate limiting reactions should be determined over a range of temperature and flow conditions. Reaction data obtained with crushed component mixtures should be compared to results using monolithic components to establish the significance of size and geometrical effects. These experiments should specifically include conditions simulating

those at the wasteform-containers interface. Finally, data will be required to establish the importance of radiolysis effects on Eh and redox behavior at repository temperatures and radiation dose rates. This data should produce bounding estimates on factors such as local  $\text{HNO}_3$  formation rates and concentrations in repository groundwater contacted with wasteform/container materials (see Issues 3.3.4.1.1/5.1.4.1 and 5.2.1.2).

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

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8. NUREG/CR-2333, "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC - Task 1, Waste Package Overview, R. Dayse, et al., B\_\_\_\_\_ M\_\_\_\_\_ I-\_\_\_\_\_, February 1982.

Issue No. 2.19.1

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: What is the production of particles and colloids (by or near the waste form) which can hold or transport radionuclides or effect waste form degradation versus time?
3. Importance of the Issue to Repository Performance

Production of particles or colloids which can hold and transport radionuclides or effect waste form performance rank as one of the priority issues in understanding major mechanisms of radionuclide releases from the repository.

The production of particles and colloids is not understood well enough to be calculated from basic principles. Nevertheless, it may be a major means of radionuclide release through groundwater transport. If it occurs extensively it can negate results predicted from models assuming solubility limitations.

4. Portions of 10 CFR 60 that are Directly Connected to the Issue

§ 60.113 Performance of particular barriers after permanent closure

(a) General provisions.

- (1) Engineered barrier system

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier

system shall be a gradual process which results in small fractional release to the geologic setting over long times. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

Very little information is known about chemically specific colloidal and particulate formation that may occur near the waste form. These will strongly depend upon the materials used in the waste package and other properties of the repository water. What is known, for instance, of iron oxide and hydroxide colloids, indicates that both leaching of the waste form and sorption and migration of radionuclides are changed in the presence of Fe colloids and particulates.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

By the time for construction authorization, DOE should have the following information:

- (a) materials and design of the waste package
- (b) groundwater composition and properties and how they are changed by interaction with the waste package
- (c) engineering tests identifying formation and properties of colloids and particulates under expected conditions
- (d) analysis and rationale for containment and controlled release mechanisms in the presence of colloids and particulates.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

Work element W1.10A addresses the problem adequately from the point of view of recognizing what variables are important in colloid and particulate formation. The document also states correctly that almost nothing is known.

8. Analysis of (7) As To Completeness, Practicality and The Likelihood of Success

The plans describing the work to be done are so general as to preclude any quantitative estimate as to their effectiveness. A much more detailed description of the actual work to be done is required in order to estimate the likelihood of success.

Issue No. 2.20.1

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: For spent fuel what are the failure mechanisms for hulls and what is their failure rate?
3. Importance of the Issue to Repository Performance

The presence of cladding hulls around fuel pellets will significantly alter the ability of repository water to contact fuel and leach out radionuclides. In order to satisfactorily quantify the source term the type and rate of hull failure will need to be evaluated.

4. Portions of 10 CFR 60 that are Directly Connected to the Issue

§ 60.113 Performance of particular barriers after permanent closure

- (1) Engineered barrier system

- (i) The engineered barrier system shall be designed so that assuming anticipated processes and events, (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional release to the geologic setting over long times.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

Spent fuel waste packages will be subjected to both aqueous corrosion and to lithostatic and hydrostatic stresses which could cause failure of the container and the cladding hulls.

Zircaloy-2 hulls are designed to be resistant to corrosion failure in reactor collants but these are dissimilar to environments anticipated in a repository. In the latter, filler materials may be interspersed between the fuel elements to act as neutron absorbers and a heat transfer medium. These fillers could cause aggressive local corrosion such as crevice attack which would be enhanced by low pH and radiolysis effects. Little is known about the local water conditions around cladding hulls and the types of corrosion to be expected over long periods of time.

Cladding hulls will also be highly embrittled during reactor operation. Ductilities as low as a ten percent in elongation have been measured in spent fuel cladding (Lowry, 1978). Large lithostatic/hydrostatic loads may cause mechanical failure of the container and the cladding, and lead to enhanced radionuclide release.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

To specify the types of corrosion and mechanical failure of hulls the following basic data will be needed:

- (a) A detailed specification of the spent fuel package design including materials in the package, temperature history, and local water conditions. Experiments will be required to characterize the corrosion failure processes so that long term estimates of hull failure rates are obtained.
- (b) An examination of the magnitude and type of loading that will be exerted on the hulls, and an analysis of the extent and rate of mechanical failure.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

Section 11.1.2.1 of the SCR addresses the aqueous corrosion resistance of cladding hulls around spent fuel pellets but there does not appear to be a plan by BWIP to credit the cladding with any containment or radionuclide controlled relocated capability. In fact, data given in Table 11-17 show that for tests at 250°C, under anoxic basalt water corrosion, a corrosion allowance to meet the 1000 year containment criterion require a Zircaloy-2 thickness of between 0.69-3.3 in. This is much larger than the cladding thickness. Therefore, cladding hulls will have little containment capability. However, based on the BWIP Work Element No. W.1.6.A. in Table 15-2 it seems that the presence of cladding material will be used in the materials interaction tests to evaluate container integrity under portotypic basalt corrosion. At this time full details of the characteristics of these tests are parameters to be measured are not specified.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

As stated in (7) above the role of cladding hulls in contribution to radionuclide containment has not been derikely addressed by BWIP. However, its influence on the behavior of surrounding barrier materials may be studied in planned interaction tests. The design of these tests, when available, will determine whether a complete design data based is likely to be obtained.

References:

1. NUREG/CR-0981, "Evaluation, Strength and Ductibility of Irradiated Zircaloy - Task 5," Lowry, A., 1978.

ISSUE NO. 2.20

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What are the transport and retardation processes and how do they affect the flux of radionuclides with time in packing materials?
3. Importance of the Issue to Repository Performance:

The waste package must be designed to contain all radionuclides during the period when thermal effects, related to decay of short-lived nuclides, are most severe. The role of the packing in retarding the movement of radionuclides from the waste form, through the waste package, to the near-field environment is an important element of the waste package design. An understanding of the potential transport and retardation processes is necessary for predictions of the flux of containment from the waste package.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue:

§ 60.111 Performance of the geologic repository operations area through permanent closure.

- (a) Protection against radiation exposures and releases of radioactive material. The geologic repository operations area shall be designed so that until permanent closure has been completed, radiation exposures and radiation levels, and releases of radioactive materials to unrestricted areas, will at all times be maintained within the limits specified in Part 20 of this chapter and such generally applicable assure that releases of radioactive materials to the accessible environment following permanent closure conform to such generally applicable environmental standards for radioactivity as may have been established by the Environmental Protection

Agency with respect to both anticipated processes and events and unanticipated processes and events.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties:

The potential mechanisms for radionuclide migration through the packing materials are: (1) transport aqueous species and colloids through pores and channels in the packing material (2) Fickian diffusion and (3) thermodiffusion (sore + effect). Migration can be retarded by reversible sorption, chemical substitution in secondary phases, precipitation and ultrafiltration, convective flow through the packing material is described in Section 5.1.1.1. <sup>Issue No 2.3</sup> Radionuclide solubility and the production of colloids are discussed in <sup>Issue No 2.12 2.14</sup> Sections 4.1 and 4.2 respectively. The uptake of radionuclides in basalt alterations products is discussed in Section 5.1.2. <sup>Issue No 2.22</sup> In this section diffusion and system in the packing material will be addressed. <sup>Issue No 2.3</sup>

Thermodiffusion (sore + effect) is a process whereby chemical species migrate down a thermal gradient. Large diffusive fluxes of sodium, magnesium and chloride have been observed in heat transfer and thermal gradient experiments involving pelagic clays, simulated waste glass and sea water (Thornton, C.). This effect may be important for radionuclides in mined geologic repositories. Fickian diffusion of radionuclides in bentonite and bentonite-quartz mixtures has been studied in several investigations. When the hydraulic gradient across the packing material is very low, diffusion is the dominant transport mechanism. Isotopes of strontium, radium, thorium, neptunium, plutonium and americium could be retained for more than 1000 years or until they decay to relatively harmless levels in a 1 meter thickness of 100% compacted bentonite or bentonite quartz mixture (Smith, M. J.; Neretnieks, I.). Attempts to measure diffusion coefficients of radionuclides in candidate packing materials have met with limited success (Apps, J. A., Torstenfelt, B.). Many of the measured values appear to be compromised by adsorption effects. Based on a review of data collected before 1982, Apps (1982) suggested that a range of diffusion coefficients of  $1 \times 10^{-10}$  to  $5 \times 10^{-10}$  cm<sup>2</sup>/sec was reasonable for modeling purposes.

Sorption of radionuclides by packing material components (bentonite, basalt) will retard the migration of contaminants. Data have been obtained at several redox potentials and temperatures (Salter, P. F.; Westsik, J. H.; Smith, M. J.). In general, radionuclides which occur predominantly as anionic ( $I^-$ ,  $TcO_4^-$ ,  $SeO_3^{2-}$ ) or neutral ( $NpO_2HCO_3^0$ ,  $UO_2CO_3^0$ ) species will be poorly sorbed by crushed basalt in the packing. Cationic species (Sr, Cs) or easily hydrolyzable (Am, Pu) species are strongly sorbed. The sorption behavior of Np, I, and Tc on basalts was found to be independent of temperature over the range of 23°C to 300°C. The sorption behavior of elements (Cs, Sr, Ra) that will precipitate or be incorporated into hydrothermal secondary alteration products at elevated temperatures is hard to assess (see Section 5.1.2). The temperature dependence of the sorption behavior of selenium, plutonium and americium is complex and poorly understood. The sorption ratio (Rd) of uranium increases with temperature over the range of 23°C to 300°C. Isotopes of strontium, cesium and americium are strongly sorbed on smectite. Uranium and technetium are moderately sorbed, whereas iodine and selenium are not sorbed at all. The reported behavior of plutonium and neptunium varied from strong to moderate sorption (Salter, P. F.; Smith, M. J.).

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

Potential production of radiocolloids in basalt-radionuclide systems has been discussed by Barney (1979) and Smith (1980). Further study of this potentially deleterious effect is important. The ability of compacted bentonite-basalt mixtures to retard radionuclide migration through ultrafiltration should also be addressed. The necessity of continued efforts to obtain reproducible sorption data at a variety of redox potentials and temperatures is relevant for waste package performance studies and modeling near-field and far-field radionuclide transport. The correction of measured diffusion coefficients for sorption effects should be attempted when high quality sorption data have been obtained.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

(TBD)

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

(TBD)

References:

1. Apps, J. A. and others, "Status of Geochemical Problems Relating to the Burial of High-Level Radioactive Waste, 1981," Draft Report, August, 1982, prepared for NRC by Lawrence Berkeley Laboratory, August, 1982.
2. Barney, G. S., Rockwell Hanford Operations, "The Kinetics and Reversibility of Radionuclide Sorption Reactions," RHO-SA-80, 1979.
3. Neretnieks, I., "Transport Mechanisms and Rates of Transport of Radionuclides in the Geosphere as Related to the Swedish KBS Concept," in Underground Disposal of Radioactive Wastes Vol. II, (Vienna, I.A.E.A., 1980) IAEA-SM-243/108, pp. 315-339.
4. Salter, P. F., Ames, L. L. and J. E. McGarrah, Rockwell Hanford Operations, "The Sorption Behavior of Selected Radionuclides on Columbia River Basalts," Informal Report, RHO-BWI-LD-48, August, 1981.
5. Smith, M. J. and others, Rockwell Hanford Operations, "Engineered Barrier Development for a Nuclear Waste Repository Located in Basalt," RHO-BWI-ST-7, May, 1980, pp. 258-272.
6. Thornton, C. C., Seyfried, W. C. and L. H. Brush, "Waste Glass - Seabed Sediment Interaction: Observations of the Soret Effect," in Workshop on the Leaching Mechanisms of Nuclear Waste Forms, May 19-21, 1982, Summary Report, PNL-4382, August, 1982, pp. 227-238.
7. Torstenfelt, B. and others, "Diffusion Measurements in Compacted Bentonite," in The Scientific Basis for Nuclear Waste Management Vol. 6, pp. 295-302.
8. Westsik, J. H. and others, "Permeability, Swelling and Radionuclide Retardation Properties of Candidate Backfill Materials," in The Scientific Basis for Nuclear Waste Management Vol. 6, S. V. Topp, Ed. (North-Holland, New York, 1982), pp. 329-336.

Issue No. 2.21

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: How do the species which incorporate radionuclides change with time in the waste package?
3. Importance of the Issue to Repository Performance:

When it is emplaced, the waste package contains a reactive assemblage of phases (e.g., glass + metal + basalt + bentonite). Such a system will convert to a more stable assemblage under the hydrothermal conditions that will prevail after repository closure. Given sufficient time, stable secondary phases will be produced; however, kinetic factors could favor the persistence of metastable intermediate phases for the entire regulatory period. The chemical and physical characteristics of these reaction products will be different than those of the original waste package. In order to predict the ability of the waste package to contain the radionuclides during the regulatory period, the properties of these metastable phases must be understood.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue:

§ 60.111 Performance of the geologic repository operations area through permanent closure.

- (a) Protection against radiation exposures and releases of radioactive material. The geologic repository operations area shall be designed so that until permanent closure has been completed, radiation exposures and radiation levels, and releases of radioactive materials to unrestricted areas, will at all times be maintained within the limits specified in Part 20 of this chapter and such generally applicable assure that releases of radioactive materials to the accessible environment following permanent

closure conform to such generally applicable environmental standards for radioactivity as may have been established by the Environmental Protection Agency with respect to both anticipated processes and events and unanticipated processes and events.

§ 60.113 Performance of particular barriers after permanent closure.

(a) General provisions.

(1) Engineered barrier system.

(i) The engineered barrier system shall be designed so that assuming anticipated processes and events (A) containment of HLW will be substantial complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractional releases to the geologic setting over long times. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of the inventory of

the radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.135 Criteria for the waste package and its components.

(a) High-level-waste package design in general.

(2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge, With Analysis of Uncertainties:

Reactions of the components of the waste package with groundwater will produce a suite of secondary minerals, aqueous species, colloids and pseudo colloids. Dissolved radionuclides and particulates were discussed in Issues No. 2.13 and 2.18, respectively. Possible changes in the chemical and physical characteristics of the waste form are described in Issue No. 2.14. The production of secondary minerals is discussed in this section.

Experimental studies of hydrothermal reactions between several waste forms, powdered basalt and groundwater from the Hanford Site are described in several recent publications (Coons, W. E.; Apted, 1981 and Komarneni, S.). These

experiments are carried out in closed reaction vessels at high temperatures (200-300°C) with a variety of rock: water ratios. During the reactions, the waste form dissolves and an assemblage of secondary alteration phases is produced. Such reactions represent an overall irreversible process which can be understood in terms of the Ostwald step rule (Apted, 1982; Dibble, W.; Fyfe, W.). The transition from the original waste form to a stable equilibrium phase assemblage proceeds via a series of intermediate, metastable products. As the system approaches equilibrium, the solubilities of the major chemical components of the system decrease.

During the experiments, the attainment of steady state was indicated by constant solution composition after 200-400 hours of reaction. Concentrations of Mo and Rb were approximately 500 and 55 ppm respectively in supercalcine reaction systems at this time. The alteration products of experiments with supercalcine, basalt and water included pollucite  $[(Cs, Na)Si Al_2O_6 \cdot nH_2O]$ , strontium molybdate and ruthenium chloride (Apted, 1981). Pollucite, powellite ( $CaMoO_4$ ) and uranionite were produced on reactions of spent fuel elements with basalt and basaltic phases (Komarneni, S.).

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

The information described in the previous section has been largely obtained from static, closed system autoclave experiments with non-radioactive materials. Data from dynamic flow experiments with radioactive waste forms with a variety of temperatures, water rock ratios, and particle sizes will be required. Similar experiments in the presence of bentonite backfill material are also necessary. The stability and leachability of the secondary alteration products produced in these experiments must be assessed under the conditions which will persist in the near-field during the period of geologic control. Information concerning the crystallographic sites of radionuclides in the alteration minerals would be useful in assessing the ability of these phases to retain the waste products.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

(TBD)

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

(TBD)

References:

1. Apted, M. J., "Hydrothermal Reactions in the System Waste Form/Basalt/  
Groundwater," in Proceedings of the 1981 National Waste Terminal Storage  
Program Information Meeting, DOE/NWTS-15, November, 1981.
2. Apted, M. J. and J. Myers, Rockwell Hanford Operations, "Composition of  
the Hydrothermal Stability of Simulated Spent Fuel and Borosilicate Glass  
in a Basaltic Environment," RHO-BWI-ST-38P, July 1982. \*(Note: B. Cook;  
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3. Coons, W. E. and E. S. Patera, Jr., "Reactions of Spent Fuel and  
Reprocessing Waste Forms with Water in the Presence of Basalt," in  
Proceedings of the 1980(?) National Waste Terminal Storage Program  
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4. Dibble, W. E. and W. A. Tiller, "Kinetic Model of Zeolite Paragenesis in  
Tuffaceous Sediments," Clay and Clay Minerals 29, 323-333 (1981).
5. Fyfe, W. S. and J. Verhoogen, "Kinetics of Metamorphic Reactions, in  
Metamorphic Reactions and Metamorphic Rocks, W. S. Fyfe, F. Turner, and J.  
Verhoogen, Eds., Geol. Soc. Amer. Mem. No. 43, pp. 53-104 (1958).
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1967-1975 (1981).

Issue No. 2.23

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: Can actinides be concentrated to increase heating in the packing materials or create a potential for criticality?
3. Importance of the Issue to Repository Performance

After loss of containment, concentration of actinides in the packing material may create a potential for a criticality. If a criticality did occur, the temperature of the immediate surrounding area may increase rapidly. Such a rapid increase in temperature may result in melting of the packing material in which the actinides had concentrated and the surrounding host rock.

4. Portions of 10 CFR 60 That Are Directly Connected To The Issue

§ 60.111 Performance of the geologic repository operations area through permanent closure.

(a) Protection against radiation exposures and releases of radioactive material. The geologic repository operations area shall be designed so that until permanent closure has been completed, radiation exposures and radiation levels, and releases of radioactive materials to unrestricted areas, will at all times be maintained within the limits specified in Part 20 of this chapter and such generally applicable Environmental Protection Agency.

(b) Retrievability of waste.

(1) The geologic repository operations area shall be designed to preserve the option of waste retrieval throughout the period during which wastes are being emplaced and, thereafter, until the completion of a performance confirmation program and Commission review of the information obtained

from such a program. To satisfy this objective, the geologic repository operations area shall be designed so that any or all of the emplaced waste could be retrieved on a reasonable schedule starting at any time up to 50 years after waste emplacement operations are initiated, unless a different time period is approved or specified by the Commission. This different time period may be established on a case-by-case basis consistent with the emplacement schedule and the planned performance confirmation program.

- (2) This requirement shall not preclude decisions by the Commission to allow backfilling part or all of, or permanent closure of, the geologic repository operations area prior to the end of the period of design for retrievability.
- (3) For purposes of this paragraph, a reasonable schedule for retrieval is one that would permit retrieval in about the same time as that devoted to construction of the geologic repository operations area and the emplacement of wastes.

§ 60.113 Performance of particular barriers after permanent closure.

- (A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.
- (B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste,

originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.131

(a) Radiological Production.

(a)(7) Criticality Control - all systems for processing, transporting, handling, storage, retrieval, emplacement and isolation of radioactive waste shall be designed to ensure that a nuclear criticality accident is not possible unless at least two unlikely, independent and concurrent or sequential changes have occurred in the conditions essentially to nuclear criticality safety. Each system shall be designed for criticality safety under normal and accident conditions. The calculated effective multiplication factor (Keff) must be sufficiently below unity to show at least a 5% margin, after allowance for the bias in the method of calculation and uncertainty in the experiment used to validate the method of calculation.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

Actinides (plutonium, neptunium and americium) from simulated waste glass have been shown experimentally (IAEA-SM-257/73, 1981) to concentrate as colloids in a porous geologic formation (glaucous sand, which is the porous layer overlying the Boom Clay formation in Belgium) when synthetic groundwater was passed over the waste glass and then through columns of the sand for periods of time ranging up to approximately 90 days.

The sand has 34% porosity, permeability of approximately  $10^{-4}$  meters/second and contains 20.8 weight percent glauconite. The flow rate of the water was 20 meters/year.

The chemical composition of the synthetic water used was the typical composition of the aquifer where the glauconic samples were collected (the water was protected from contact with the atmosphere to control redox and pH) and is shown below:

### Water Composition (mg/l)

Ca <sup>2+</sup> = 3.03	Cl <sup>-</sup>	6.4
Mg <sup>2+</sup> = 3.2	SO <sub>4</sub> <sup>-2</sup>	0.5
Fe <sub>tot</sub> = 0.1	CO <sub>3</sub> <sup>2-</sup>	201
Na <sup>+</sup> = 55.3	pH	8.35
K <sup>+</sup> = 7.71	Eh	150 mV

The quantity of actinide colloids collected by porous geologic media will depend on the pore size of the media. In the experiment described, 7 and 15 percent of the leached plutonium activity and 40 and 100 percent of the leached americium activity was retained on filters with porosities of 1 micron and 0.1 micron, respectively.

There is uncertainty in applying the experimental data cited above to concentration of actinide colloids in a porous geologic media of a basalt repository. The data apply only to one set of conditions rather than to a range of conditions. Also, the concentration of actinide colloids can depend on the design of the repository and the waste packages. For example, a packing material could be designed to tailor the chemistry of the groundwater and the rate of flow to minimize leaching and to minimize actinide colloids. Carbonates in groundwater are believed to form soluble anionic complexes with the TRU nuclides. The redox potential (Eh), pH and chemical water composition will affect the physico-chemical states (electrical charge) of the nuclides. The charge will determine the partitioning of the nuclides between the colloidal and soluble phases. Conversely, the groundwater flow rate controls the rate of travel of the colloids and their subsequent dissolution. It also may be filtered to remove actinide colloids after passing over each waste package or to arrange the storage array to minimize the concentration of these colloids.

#### 6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

The potential for a nuclear criticality could affect the design of the repository. For example, it may not be possible to position spent fuel

packages in horizontal columns, end to end. By the time of construction authorization, DOE should have the following information:

1. The transport mechanism and rate of transport of actinides from spent fuel in a saturated repository under the expected conditions of Eh, pH, groundwater chemistry and flow rate. This information should be extrapolated for periods of time from zero to 10,000 years.
2. Based on the above, the quantities of plutonium, americium and neptunium colloids expected to be transported from a column of failed fuel packages over the same time period.
3. The largest quantity of actinides expected to concentrate in a porous geologic media and the geometry of the concentrated volume.
4. A nuclear safety analysis for this scenario.
7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

BWIP is conducting laboratory experiments to determine the solubilities and colloidal formation of key radionuclides (the actinides and transurancs in particular) under conditions applicable to a basalt repository. Data from these investigations will be used to estimate the release of radionuclides in the repository.

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success

We believe it is possible to conduct an experimental program that will yield the information necessary to predict the rate of release of radionuclides from the repository. However we cannot predict the success of such programs on the basis of the information provided in the SCR.

An analysis of BWIPs planned approach in (7) for estimate the release of radionuclides in the repository can be made only after review of BWIPs detailed test plans and detailed plan for analysis of the information.

The BWIP SCR (Work Element W...1.10.A) shows intent to determine the formation and stability of radionuclide complexes and/or colloids over expected repository near field and far field conditions.

Although the potential criticality hazard of waste packages are addressed, the SCR does not address the potential criticality hazards associated with concentration of actinide colloids in a porous geologic media (in formation items 6.2, 6.3 and 6.4 above.

## References

1. IAEA-SM-257/73, Underground Migration of Long-Lived Radionuclides Leached From A Borosilicate Glass Matrix, A. Avogadro, C. N. Murray, A. DePiano, G. Bidoglio, International Symposium On Migration in the Terrestrial Environment of Long-Lived Radionuclides from the Nuclear Fuel Cycle, Knoxville, Tennessee, July 27-31, 1981.

Issue No. 2.23

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: How do radionuclides migrate through failed containers and how does this change with time? (Relate to Issue No. 2.5)
3. Importance of the Issue to Repository Performance

The migration of radionuclides through failed containers and the change of this process with time must be understood and known to evaluate the relevance of this migration with respect to performance of engineered barriers system after permanent closure.

4. Portions of 10 CFR 60 that are Directly Connected to the Issue

§ 60.113 Performance of particular barriers after permanent closure

(a) General provision.

(1) Engineered barrier system.

(i) The engineered barrier system shall be design so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractuinal releases to the geologic setting over long time. In the case of disposal in the saturated zone, it shall be assumed in designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

- (A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.
- (B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally placed in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.135 Criteria for the waste package and its components

(a) High-Level Waste package design in general

- (1) Packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.
- (2) The design shall include but not be limited to consideration of the following: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

Present state of knowledge on chemical and physical property changes in container materials and properties are discussed in Issue No. 2.5 and on the flux of radionuclides in Issue 2.20. Production of particles and colloids which can hold or transport radionuclides are covered in Issue 2.18. However, little is known on radionuclide migration after container failures.

6. Summary of the Additional Information Needed to REsolve the Issue By the Time of Construction Authorization Application

Radionuclides which migrate through failed containers together with any chemical and physical changes they may undertake and/or by-products formed must be identified and quantified. The paths of transport and possible reactions with materials they come into contact with a different time periods must be understood to determine the release of these radionuclides to the repository environment.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

References:

Issue No. 2.26

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: Does alpha radiation in the waste packing materials affect solution chemistry and hence transport and species identification?
3. Importance of the Issue to Repository Performance

The bentonite/basalt packing is designed to retard radionuclide transport by sorptive processes (Wood 1982). The performance of a sorptive barrier depends upon local chemical conditions and the speciation of ions in the solution. It has been demonstrated that solution chemistry and the speciation of multivalent TRU elements can be selected by alpha-radiolysis. Consequently, a thorough assessment of retardation in the packing must consider whether the radionuclides will exhibit increased mobility due to alpha radiolysis effects. This issue is related to the general question of establishing the significance of radiolytic effects on waste package performance (Issue 2.10).

4. Portions of 10 CFR 60 that are Directly Connected to the Issue

§ 60.113 Performance of particular barriers after permanent closure

(a) General provision.

(1) Engineered barrier system.

(i) The engineered barrier system shall be design so that assuming anticipated processes and events (A) containment of HLW will be substantially complete during the period when radiation and thermal conditions in the underground facility are dominated by fission product decay; (B) any release of radionuclides from the engineered barrier system shall be a gradual process which results in small fractuinal releases to the geologic setting over ling time. In the case of disposal in the saturated zone, it shall be assumed in

designing the engineered barrier system that partial or complete filling with groundwater of all available void spaces in the underground facility occurs.

(ii) In satisfying the preceding requirement, the engineered barrier system shall be designed, assuming anticipated processes and events, so that:

(A) Containment of HLW within the HLW waste packages will be substantially complete for a period of 1,000 years after permanent closure of the geologic repository, or such other period as may be approved or specified by the Commission.

(B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay.

§ 60.135 Criteria for the waste package and its components.

(a) High-level-Waste package design in general.

(1) Packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.

(2) The design shall include but not be limited to consideration of the following factors: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, mechanical strength, mechanical stress, radiolysis, radiation damage, radionuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

5. Summary of the Present State of Knowledge with Analysis of Uncertainties

Reasonably extensive literature exists on alpha-radiolysis effects in pure water (Draganic, 1971). Alpha particles, by virtue of their greater linear energy transfer, have somewhat greater yields than gamma rays for molecular decomposition products of water (i.e.,  $H_2$ ,  $H_2O_2$ , etc.). Fundamentally, however, the effects are similar: for both gamma rays and alpha particles, it is ionization which is responsible for the radiolytic effects in solution. Due to the short range ( $\sim 40m$ ) of alpha particles in water, however, alpha-radiolysis effects will be restricted to the immediate vicinity of the migrating radionuclides.

Direct measurements (Fried, Rai) indicate that both solution pH and the speciation of plutonium can be affected by solution alpha-radiolysis effects. Specifically, the pH decreases, possibly due to nitric acid formation from atmospheric nitrogen in the presence of moisture. Plutonium (III) is said to undergo successive radiolytic oxidations to plutonium (VI), followed by cyclic oxidation-reduction behavior. This behavior has been interpreted in terms of air initial oxidizing affect of OH radical and a subsequent reducing effect of  $H_2O_2$ : Swedish workers (Christensen, H., 1982) have recently calculated that alpha and gamma radiolysis can oxidize Fe(II) to Fe(III) in Swedish repository groundwater.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application

While the available evidence indicates that radiolysis may produce an oxidizing environment under certain conditions, the significance of this affect in radionuclide retardation in the packing (and on waste package performance in general) has not been established. Major uncertainties involve the relative contribution of radiolysis effects in comparison to other reactions and processes which may occur in the backfill. Specifically, it must be determined to what extent radiolytically-induced changes in pH and redox behavior will be offset or swamped by the buffering properties of the backfill. For example, if radiolytically-produced oxidants (e.g., OH radical) are effectively scavenged

by iron in the basalt or by dissolved  $H_2$ , radiolysis effects on redox behavior could be negligible. To determine the significance of radiolysis, effects in the packing data will be needed to estimate the relative formation and scavenging rates for radiolytically-produced species under repository conditions. This should include the effects of temperature and radiation dose rate. In particular, for alpha radiolysis the dose rate will depend critically upon the postulated distribution(s) of migrating TRU elements in the packing.

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6)

Radiation effects studies are to be carried out largely in conjunction with a program of <sup>hydro</sup>hydro-thermal testing incorporating actual waste forms and palicale materials this phase of the testing program is to be carried out in a hot cell, also the radiation environment will be provided by the waste form material. (Work element W.1.3.A) In these tests, solution chemistry measurements will be carried out during the tests, and reaction products will be examined afterwards. Presumably, results will be compared with those obtained in the absence of irradiation to determine if irradiation noticeably affected solution or material properties. No specific comparisons or analytic technique unique to testing for irradiation effects are described in the work element. Presumably, again, techniques and parameters monitored are to be similar to those in the hydrothermal experiments without irradiation (i.e. Eh, pH, characterization of alteration products, determination of elements concentration in solution, etc.)

Other studies are cited in element W.1.3.A. in which corrosion testing is to be carried out in a gamma field, and backfill and buffer materials are to be subjected to external gamma irradiation. The test conditions are not explicitly defined; these appear to be scoping type tests. Finally work elements W.1.10.A refers to investigations of the possible effects of the radiation gillco on radionuclide geochemical behavior, involves radionuclide complexing and colluid formation. No specific plans or techniques are presented.

8. Analysis of (7) As To Completeness, Practicality and The Likelihood of Success

At this point, descriptions of the planned approach are very general; it is not clear to what extent, if any, alpha radiolysis effects are to be treated as a separate issue. In general terms the planned approach correctly recognizes the possibility that solution chemistry and radionuclide speciation might be modified by radiation effects. The problem is to be addressed by a sense of what appear to be largely scoping experiments. These may be incomplete in two respects: First it is not clear that the hydrothermal scoping experiments will include worst case conditions. For example, if the effects of solution radiolysis and of geochemical interactions oppose each other, as has been postulated, the relative rates of the two processes are critical factor. For radiolysis processes, the rate will depend upon local radiation dose rate. And total dose, for example radiolysis in particular, these will depend on the detailed distribution of radionuclides in the test facility. The mechanism of x-radiolysis may also be somewhat different from gamma-radiolysis. Strict equivalence cannot always be assumed. In short, it is not clear that the hydrothermal experiments will bound the extent to which radiolysis effects may occur before geochemical control sets in under field conditions. Second, there is no specific mention of how the significance of x-radiolysis effects on radionuclide speciation and complexing will be determined, particularly for conditions subsequently to the thermal period.

The practicality of carrying out Eh determinations under hydrothermal conditions, in all inhomogeneous system, in a radiation field sufficiently intense to simulate repository conditions remains to be determined. Specific techniques are evidently under development. This is a possible weakness of the approach, in that the major initial radiation test involves a fairly complex facility, incorporating many interactions and somewhat limiting the \_\_\_ of radiological variables. (likelihood of success might be increased by scoping measurements on simpler systems.

## References

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2. Draganic, I. G. and Z. D. Draganic, The Radiation Chemistry of Water, Academic Press, New York, 1971.
3. Fried, S. and others, "The Effect of Radiation on the Oxidation States of Plutonium in Various Aqueous Solutions," in Scientific Basis for Nuclear Waste Management, C. M. Northrup, Ed., Plenum Press, New York, 1980, p. 655.
4. Rai, D., R. J. Serne, and D. A. Moore, Soil Sci. Soc. Am. J. 44, 490-495, 1980.
5. Wood, M. I., "Experimental Investigation of Sodium Bentonite Mobility in Hanford Basalt," Rockwell Hanford Operations, Paper D 11.8, Symposium D., Materials Research Society Annual Meeting, Boston, Massachusetts, November 1982 (in press).

1. Name of the Site: BWIP - Handford Site
2. Statement of the Issue:  
~~5-3-1-~~ What are the conditions which affect criticality?
3. Importance of the Issue to Repository Performance:  
(same as for issue ~~5-3~~)  
2-22
4. Portions of 10 CFR 60 That Are Directly Connected To The Issue:  
(same as for issue ~~5-3~~)  
2-22
5. Summary of the Present State of Knowledge, With Analysis of Uncertainties:

In order for a mass of fissile material to achieve and maintain a critical chain reaction, several conditions must be met simultaneously, e.g., the proper geometric configuration, the presence of a neutron moderator and reflector and the absence of neutron poisons. Redistribution of the fissile material in the waste package or package, either within the canister or external to it, into a more optimum configuration is the prime requisite in achieving criticality. The only mechanisms deemed significant to redistribution are intrusion of groundwater and a severe natural phenomena, such as an earthquake, must bring together over 40 spent fuel canisters with into an optimum, close-packed arrangement, free of neutron poisons. Otherwise, several uncontrolled natural events must occur in a proper sequence and within a specific period of time. These are:

- a. Water must enter the repository in the required volume.
- b. The waste canister and/or cladding must fail.
- c. The matrix in which the fissile isotopes are held, i.e., glass for the high level waste and the sintered oxides for the fuel elements, must be physically removed or destroyed, or selective fissile isotopes leached out (as long as the fuel material remains homogeneously distributed it will not go critical). Fissile plutonium must enter the leachout as a colloid.
- d. The packing material surrounding the waste packages is absent (never placed or washed away).
- e. After flowing for long periods of time over a series of waste packages with exposed spent fuel or solidified high level waste, the leachout passes through an intact plug of clay.

- f. The fissile plutonium colloids are filtered by the clay and retained, so that over a long period of time a critical mass is accumulated on the clay in an optimum geometric configuration.
- g. Water is present in quantities sufficient to moderate and reflect neutrons so that a criticality occurs.
- h. Neutron poisons are absent.

6. Summary of the Additional Information Needed to Resolve the Issue By the Time of Construction Authorization Application:

7. Summary of the Planned Approaches to Testing, Tests, Test Methods, and Investigations to Provide the Information Needs of (6):

8. Analysis of (7) As To Completeness, Practicality and Likelihood of Success:

References: