

APPENDIX I
DRILLING MUD EFFECTS ON HYDROGEOLOGIC TESTING

01/28/83

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BWIP DSCA/APP I/LOGSDON

1 INTRODUCTION

The majority of the deep test wells referenced in the report "Site Characterization Report for the Basalt Waste Isolation Project" (SCR) were drilled using mud rotary drilling techniques. Many of these wells were tested for hydraulic properties. Section 5.1.3.1 of the SCR describes the hydrologic test methods utilized. The effects of drilling mud on the results of the hydraulic testing program are not discussed in the SCR, although these so-called "skin effects" may induce erroneous test results which can constitute to a non conservative assessment of groundwater flow. The SCR presents no plans to correct for the effects of drilling mud in future hydrogeologic testing.

The purpose of this report is to evaluate the extent to which drilling mud effects may have affected the results of hydrogeologic testing as reported in the SCR and to present the background for this evaluation. The objectives are to: 1) describe the mud invasion problems associated with mud rotary drilling in basalt, 2) evaluate the literature that prescribes methods of correcting negative effects of drilling mud on hydraulic test results, and 3) evaluate the potential effects of drilling mud on the test results presented in the SCR.

2 DRILLING MUD EFFECTS

Drilling mud transport from the borehole into the surrounding basalt occurs because during drilling the hydraulic head within the borehole is greater than the hydraulic head in the surrounding formation. The drilling mud often has a high density; mud level is maintained at land surface to facilitate removal of drill cuttings. The hydraulic head of the drilling mud thus creates an outward gradient from the borehole. Drilling mud migration into the basalt is dependent on the hydraulic conductivity of the material surrounding the borehole, the physical and chemical characteristics of the mud and the drilling time.

Details concerning the physical and chemical characteristics of the muds used and the extent of mud migration into the basalt units at the Hanford site are not available in the SCR. Data on the rate of mud loss reportedly were

collected by Rockwell Hanford Operations (RHO) on some of the test wells. These data are not presented in the SCR.

Well development is a standard practice used to reduce formation damage caused by drilling near a completed well. Development procedures include physical and chemical actions to remove drilling mud and cuttings from the formation. The density and viscosity characteristics of the mud make it very difficult to remove from the formation. Full rehabilitation of formation damage from clay based drilling muds is normally not possible (Abrams, 1977).

Two distinct well development techniques have been utilized by RHO (personal communication with RHO hydrologists, 7/82). Flowing wells are allowed to free flow until the drilling mud no longer emanates from the well. Fluorescein dye is used as a tag to determine when drilling mud is no longer being removed from the borehole. A second technique utilized by RHO involves direct pumping either by airlift or other means to remove drilling mud from the borehole. River water is added to some wells to facilitate well development; these wells have yields too low to make their development practical under natural conditions. Trisodium phosphate also has been used by RHO to enhance removal of clays used in the drilling muds from the borehole and the basalt immediately surrounding the borehole. Well development is very dependent upon the ability of the test interval to produce sufficient water at a high enough velocity to flush the drilling mud from the rock near the borehole.

3 EFFECTS OF DRILLING MUD ON MEASUREMENT OF HYDRAULIC PROPERTIES

Significant research has been conducted on the effects of drilling muds on well testing for hydraulic properties in the petroleum industry. Abrams (1977, p. 586) noted that a number of previous investigators have found that:

1. Invasion and formation damage occur with all muds.
2. The depth of invasion and level of impairment can be controlled, to a certain degree, by designing the mud to include bridging material.

3. The effectiveness of the bridging material in reducing invasion is a function of the concentration and practice size of the material and of the pore sizes of the formation rock.
4. Damage is most likely to occur in higher permeability formations; most muds contain sufficient quantities of particles, including cuttings, in the size range required to bridge lower permeability rocks.
5. Where invasion occurs, backflushing does not remove the impairment.

The invasion of drilling mud into the basalt surrounding a borehole reduces the hydraulic conductivity near the borehole. Hydrogeologic testing involves the measurement of friction losses within the formation resulting from the flow of water to or from the borehole. The drilling mud effect or "skin effect" can impact test results dramatically.

Numerous articles are available in the petroleum field which describe various procedures for determining the significance of the skin effect or drilling mud effect on hydraulic testing and on quantifying the skin effect. Some useful references are: 1) Earlougher (1977) - review of basic principals; survey of well testing techniques, 2) Gringarten et al (1979) - constant flow rate tests with wellbore storage and skin effects, 3) Ramey et al (1975) - slug tests with wellbore storage and skin effects, and 4) Brereton (1979) - improved method for step drawdown tests.

One of the most basic equations describing the skin effect is

$$H_w = BQ + CQ^n$$

where: H_w = hydraulic drawdown, B = a time dependent coefficient describing friction or head losses in the aquifer, Q = pumping rate, C = coefficient describing laminar and turbulent friction or head losses near the well including the skin effect, and n = an empirical constant (Ramey, 1982). The typical methods for determination of aquifer parameters from single hole tests include the assumption that the CQ^n portion of the equation is equal to zero. Drilling mud effects can make this portion of the equation very significant.

A clear distinction should be made between "linear" well loss resulting from a low permeability skin (skin effect) and well loss resulting from "nonlinear" flow. Linear flow is defined as laminar flow for which Darcy's law is valid. In the petroleum literature, the linear head loss (H_{L1}) across a borehole skin is related to a dimensionless skin factor(s) as follows:

$$H_{L1} = Q/2\pi T (s)$$

where T is aquifer transmissivity. Nonlinear flow is defined by flow conditions for which Darcy's law is not valid. This includes laminar flow with large inertial forces and turbulent flow. In the petroleum literature, the head loss resulting from nonlinear flow (H_{L2}) is given by the following empirical equation:

$$H_{L2} = DQ^2/2\pi T$$

where D is an empirical constant. The hydrology literature makes no mathematical distinction between skin effects and nonlinear head loss. The two effects are combined and described as a total well loss (H_L) by the following empirical equation:

$$H_L = H_{L1} + H_{L2} = CQ^n$$

where C and n are as defined earlier.

4 RHO HYDRAULIC TEST METHODS

Section 5.1.3.1 of the SCR describes the hydrologic test methods used for BWIP. Figure 5-5 on page 5.1-15 indicates that different test procedures are used if the water level response after packers are set is slow or intermediate to fast. However, nowhere in chapter 5 are the analysis procedures described. Consequently it is impossible to determine from the SCR whether petroleum based analysis techniques that include analysis of and correction for skin effects have been applied. RHO hydrologists (personal communications, 7/82) have indicated that analysis for skin effects was conducted on data from some of the sites. But such corrections are not discussed in the SCR.

An important aspect of well testing is the effective radius of influence of the test. A short term test of the type that dominates the BWIP testing program affects a much smaller radius of influence than a long term test. The radius of influence relative to the area of mud penetration is important with respect to evaluating the mud effects on testing results. RHO hydrologists (personal communication, 7/82) have indicated that late data from air-lift recovery tests were used wherever possible to eliminate or minimize the mud effects. Therefore, it is probable that hydrogeologic parameters calculated from long term recovery tests are more valid than results from short term pulse or constant head tests.

It is not possible to evaluate accurately the drilling mud impacts on the values of effective hydraulic conductivity presented in Chapter 5 of the SCR with the available information. The results from short-term tests probably reflect both the characteristics of mud invasion and the properties of the

aquifer. Consequently considerable uncertainty is introduced into all of the hydraulic parameter results presented in the SCR.

References

1. Abrams, A., 1977, Mud design to minimize rock impairment due to particle invasion: *Journal of Petroleum Technology*, May p. 286-592.
2. Agarwal, R. G., Rafi Al-Hussainy, and H. J. Ramey Jr., 1970, An investigation of wellbore storage and skin effect in unsteady liquid flow: I. Analytical treatment: *Society of Petroleum Engineers Journal*, Vol. 10, September, p. 279-297.
3. Brereton, N. R., 1979, Step drawdown pumping test for the determination of aquifer and borehole characteristics: Technical Report TR103, Resources Division of Water Resource Center, Medmenham Laboratory, England, 26 p.
4. Earlougher, R. C., 1977, Advances in well test analysis: *Society of Petroleum Engineers of AIME*, Dallas, 264 p.
5. Glenn, E. E., and M. L. Slusser, 1957, Factors affecting well productivity: II. Drilling fluid particle invasion into porous media: *Petroleum Transactions, AIME*, Vol. 210, p. 132-139.
6. Gringarten, A. C., D. P. Bourdet, P. A. Landel, and V. J. Kniazeff, 1979, A comparison between different skin and wellbore storage type-curves for early-time transient analysis: *Society of Petroleum Engineers of AIME*, SPEC 8205, 17 p.
7. Lohman, S. W., 1972, Ground-water hydraulics: *U. S. Geological Survey Professional Paper* 708, 70 p.
8. Matthews, C. S., and D. G. Russell, 1967, Pressure buildup and flow tests in wells: *Monograph Vol. 1, Henry L. Donerty Series*, *Society of Petroleum Engineers of AIME*.

*Not all of these references are cited in this report. The ones that are not cited are presented for the assistance of the reader who may wish to pursue this subject further.

Appendix J
Reserved

APPENDIX K

**Site Issue Analyses Related to the Nature of
the Present Groundwater System at
the Hanford Site, Washington**

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1 INTRODUCTION

The importance of understanding the nature of the groundwater systems of the Hanford site is stated clearly by DOE:

"It is generally recognized that the most probable mode by which radio-nuclides could be released from a repository facility is through the groundwater system" (SCR, page 12.1-1).

The combination of innate complexity and inadequate site characterization at the Hanford site was summarized by William Twenhofel of the Hydrology and Geology Overview Committee of the Basalt Waste Isolation Project:

"The data to date on the subsurface hydrologic flow system of the Hanford Reservation are most puzzling. I can only conclude: (1) some of the head data are in error, or (2) The flow system is so complex that it will never be able to be properly characterized for eventual licensing. I do not believe it will be possible to develop credible risk assessment models without characterizing the flow system" (Domenico et al., 1981, page VI-9).

The NRC staff also regards a quantitatively adequate characterization of the nature of the present groundwater flow system at the Hanford site to be indispensable to the evaluation of licensing issues related to proposed 10 CFR 60. Selected groundwater issues of major significance with respect to the SCR are discussed in Chapter 4 of this NUREG. The Site Issue Analyses (SIA's) reproduced in this appendix support and expanded on the issues discussed in Chapter 4. These SIA's include analyses of the following major topics: (1) the three-dimensional distribution of hydraulic parameters; (2) boundary conditions for the flow system; (3) potential effects of structural and stratigraphic discontinuities on groundwater flow; (4) the use of hydrochemistry for characterization of groundwater flow; (5) the DOE's conceptual model of groundwater flow; and (6) the DOE mathematical models of groundwater flow. The complete set of SIA documents is located in the NRC Public Document Rooms.

Issue No. 1.1

1. Name of the Site: Basalt Waste Isolation Project (BWIP) - Hanford, Washington
2. Statement of the Issue: What is the nature of the present groundwater system?
3. Importance of the Issue to Repository Performance

A knowledge of the nature of the groundwater system is required for evaluation of the performance of any repository. This performance evaluation is critical to the licensing process.

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

60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

Specifically, 10 CFR 60 requires

- o evaluation of radionuclide release for comparison with the EPA standard (\$60.112 - Performance Objective)
- o evaluation of undisturbed groundwater travel time (\$60.113(a)(2) - Geologic Setting)
- o evaluation of a wide range of potentially favorable and unfavorable conditions (\$60.112(b) and (c), respectively).

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

Present State of Knowledge

The groundwater flow system is not adequately understood at this time. The directions and velocities of flow in the presently existing system cannot be assessed utilizing existing data, and it is not possible to make any of the evaluations of repository performance which depend upon hydrogeology. These evaluations depend upon an understanding of the components of the groundwater system which are discussed in the following site issue analyses:

- o parameters (1.1.1)
- o recharge and discharge locations (1.1.2)
- o boundaries (1.1.3)
- o structural heterogeneities (1.1.4)
- o stratigraphy and lithology (1.1.5)
- o hydrochemistry (1.1.6)

These components must also be organized into a conceptual model of the system, which is discussed in SIA 1.1.7. This model can then be used for mathematical analysis, as discussed in SIA 1.1.8.

Uncertainties

The present uncertainty about the nature of the groundwater system derives from the uncertainties in the components. Parameters and heads are known only within very wide ranges, and some important parameters are not known at all. Boundary conditions, including recharge and discharge locations, have not been investigated in the field. The hydrogeologic significance of known structural heterogeneities is unclear, and it is not known whether all significant heterogeneities have been identified. The significance of stratigraphy and lithology within the flow systems has not been demonstrated. The hydrochemistry cannot be uniquely interpreted.

Because of these uncertainties, the conceptual model of the groundwater systems is uncertain, and thus mathematical modeling remains highly speculative.

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

Several key sets of information are needed to allow development of an acceptable understanding of the nature of the groundwater system. A reliable knowledge of the present groundwater heads must be obtained, both in three dimensions and over time. This information is needed to allow evaluation of existing flow directions, and to allow calibration of the mathematical model for steady-state conditions. Information is required about the behavior of the system when it is subjected to a large-scale hydrogeologic stress. This is required for calibration of the mathematical model under both steady and nonsteady-state conditions. Values of horizontal and vertical hydraulic conductivity appropriate to repository scale do not exist and are required for performance assessment. The porosity of the host rocks is presently almost unknown. Retardation and dispersion behavior are also inadequately known. Matrix diffusion behavior and parameters have not been evaluated, despite the possibility that this mechanism may have a major positive effect on repository performance.

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

The planned approaches to evaluating the present groundwater system are essentially a continuation of the previous testing program. Primary emphasis will remain on temporary completions in single boreholes to obtain further information about heads, horizontal hydraulic conductivities, and hydrochemistry. In addition, several dual-borehole tests are planned within the Cold Creek Syncline and one cluster test is planned at a site immediately south of the RRL site. While a general description of the proposed testing program is presented in the SCR and supporting documents (BWIP 1982a, 1982b and 1982c), details are lacking. Additional tests will be conducted in portholes and possible room-scale environments within the exploratory shafts. Several tracer tests are planned to evaluate effective porosity and dispersivity, although locations and test details are not specified in the SCR. Boundary

conditions will be evaluated using hydrogeologic test data and the results of regional models. Hydrochemical samples will be taken during the single borehole drill-and-test sequence and from selected zones in existing holes using double packer systems. The effects of geologic discontinuities and structures upon groundwater flow will be evaluated using results of limited-scale hydrogeologic tests, hydraulic head measurements and hydrochemistry. DOE plans to perform numerical modeling at various scales to resolve all other questions about boundaries, flows, and to validate the conceptual hydrogeologic model.

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

The NRC staff includes that the proposed test plan will not provide adequate definition of the groundwater system. This conclusion is drawn from the conclusions of the contributing site issue analyses (1.1.1 through 1.1.8) and is based primarily upon the following factors:

- o Head distributions developed from temporary completions are too inaccurate to allow the flow system to be identified.
- o Hydraulic conductivities developed from tests in single boreholes vary widely and only represent a small sample of the hydrogeologic system. The values are inappropriate for use in performance evaluation because they do not allow development of sufficient confidence in the results.
- o Models used for evaluation of repository performance will not be calibrated for steady-state conditions because of the lack of accurate head data, or in the transient case because of the lack of sufficient area-scale pump or stress tests. Performance modeling is not reliable without such calibration.
- o Fluid and solute transport parameters will not be sufficiently quantified by the proposed test program.

The NRC staff regards large-scale testing of this site as essential. Such testing is feasible at this site (Appendix E) and is considered to be the normal test approach for site evaluations (as distinct from reconnaissance). A limited number of such tests would provide much of the data which the NRC staff has identified as lacking. The staff also considers that one such test should be conducted at the center of the repository location, to provide a hydraulic analogue of repository performance. This test would directly address many of the repository performance questions, and would reduce uncertainty about behavior of the groundwater system.

Issue No. 1.1.1

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What is the three-dimensional distribution of hydrogeologic parameters (including vertical and horizontal hydraulic conductivity, hydraulic head, effective porosity, double porosity, dispersivity, and matrix diffusion)?
3. Importance of the Issue to Repository Performance

The three dimensional distribution of hydrogeologic parameters is necessary for formulating and calibrating groundwater models for performance evaluation.

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

60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

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

Present State of Knowledge

Hydrogeologic parameters have been measured primarily from single-hole tests using packer technology. Numerous measurements of horizontal hydraulic conductivity and hydraulic gradient have been obtained in interflow zones. Some measurements of horizontal hydraulic conductivity have been made in dense basalt zones. No measured values of vertical hydraulic conductivity exist. Two tracer tests have been conducted at one location in one zone to measure effective porosity and dispersivity. Matrix diffusion has not been measured. A high degree of variability exists in the measured parameters, making interpolation between measured values unfeasible at this time using normal interpolative methods.

Uncertainties

The accuracy and bulk representativeness of measured data are uncertain because of potential problems associated with using packer technology for hydraulic head measurement (Appendix G), drilling mud (Appendix I), the large variability of data (Appendix H) and the lack of large-scale tests for bulk parameters (Appendix E). There is a high degree of uncertainty associated with the use of normal interpolative methods to develop the three-dimensioned distribution of hydrogeologic parameters due to the uncertainties associated with the measured data.

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

Representative bulk values of hydraulic parameters are required at a scale appropriate for performance assessment. Accurate long-term measurements of hydraulic head are also necessary. An interpolative method to define the three-dimensioned distribution of parameters must be developed and validated.

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

Additional testing of hydraulic parameters and measurement of hydraulic heads are planned in single boreholes using packer technology. Several dual-borehole tests and at least one multiple-hole test are also planned. Specific details of the planned tests are not given in the SCR. Tests for hydraulic parameters are planned from the exploratory shaft and underground test facility. The detailed methodology by which measured data will be used to develop the three-dimensional distribution of hydrogeologic parameters is not presented in the SCR. The SCR indicates that an iterative process between data collection and modeling will be used to establish additional data needs.

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

The NRC staff includes that primary emphasis on single-hole tests using packer technology and the limited number of multiple-hole tests will not provide sufficient bulk hydrogeologic parameters for repository performance evaluation. The NRC staff considers that short-term monitoring of hydraulic head using packer technology is inadequate and that long-term monitoring using conventional methods is necessary. It is also important to consider matrix diffusion, since this could have a positive effect upon repository performance. Integration of measured data into a three dimensional distribution of parameter values is not currently feasible due to large variations in measured values and uncertainty in their bulk representativeness. The iterative process described to establish additional data needs is considered very appropriate. However, it does not appear that the proposed plans contain enough large-scale tests to permit adequate development of the three-dimensional parameter distribution.

Issue No. 1.1.1.1

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What are the measured hydrogeologic parameters of each unit tested?

3. Importance of the Issue to Repository Performance

Formulation of defensible groundwater models for performance evaluation, and development of a continuous three-dimensional distribution of parameters for use in those models require a data base of representative hydrogeologic parameters obtained by in situ testing.

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

60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

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

Present State of Knowledge.

Values of horizontal hydraulic conductivity are primarily from single-hole tests in flow tops, with some values from dense basalt zones. One multiple-hole test in DC-7/8 yielded a bulk value representative of a scale of at least 15 meters (50 feet). Present data are extremely variable, even within the same stratigraphic unit tested at different locations (Appendix H). Based on these test results, flow tops are significantly more permeable than dense basalt zones. No values of vertical hydraulic conductivity have been measured. Effective porosity is on the order of 10^{-4} based on only two tracer tests over a distance of approximately 15 meters (50 feet) in an interflow breccia in DC-7/8. Dispersivity, based on the same DC-7/8 tests, is 0.8m (2-3 feet). No data on matrix diffusion coefficients are available. Hydraulic head has been measured within a number of test intervals using packer technology to obtain hydraulic isolation.

Uncertainties

Analysis of uncertainties considers only horizontal hydraulic conductivity effective porosity, dispersivity and hydraulic head. Measured horizontal hydraulic conductivity has a high degree of uncertainty because of short duration tests on single wells drilled using mud rotary techniques. Effective porosity and dispersivity have been measured at only one site, over a very limited lateral distance. Uncertainties in hydraulic head result from the lack of long-term data, possible disturbances caused by drilling and testing, and measurement using packer technology. It is our belief that much of the variability and uncertainty has been introduced by the method and scale of testing.

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

Bulk values of horizontal and vertical hydraulic conductivity need to be measured using appropriate tests (e.g., see Appendix E). A data base needs to be established for effective porosity, double porosity, dispersivity, and matrix diffusion coefficient. Measurements that represent stable long term hydraulic head are required. All parameters should be measured at the scales required for performance assesment.

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

Additional measurements of hydraulic parameters and hydraulic heads are planned in selected intervals of the Saddle Mountain, Wanapum and Grande Ronde Basalts. The great majority of these tests are to be in single boreholes using packer technology. Several dual-borehole tests are planned within the Cold Creek Syncline (e.g., DC-1/2, DC-4/5, DC-7/8), and one cluster test (multiple bore-hole) is planned immediately soth of the RRL site (DC-16, A, B, C).

One large-scale test is planned in the Cold Creek Valley, some 10 kilometer (6 miles) from the RRL. A general description of these plans is provided in the SCR and supporting documents (BWIP 1982a, 1982b and 1982c). Vertical hydraulic conductivity will be determined in multiple-hole tests using the ratio method (Neuman and Witherspoon, 1972). Specific zones to be tested are not described in the SCR. The SCR indicates that permanent installations for monitoring hydraulic head are being considered, although further details are not provided. Tracer tests are planned to evaluate effective porosity and dispersivity. Plans for evaluating matrix diffusion and double porosity are not provided. Some hydraulic testing is planned in the exploratory shaft and underground test facility (pages p. 17.2-26 to 28), however, no details are provided.

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

It is difficult to evaluate the previously described planned approaches because no details are presented in the SCR. However, the plans appear to place primary emphasis on single-hole tests using packer technology. The NRC staff feel the limited number of multiple borehole tests (DC-1/2, DC-4/5 and DC-7/8, and DC-16A, B and C) and the relatively small volume of the medium to be tested will not provide sufficient bulk hydrogeologic parameters for the performance evaluations required by 10 CFR 60. It is also questionable whether the information gathered during the planned large-scale test will be transferred to the site. DOE's plans are incomplete because plans to evaluate matrix diffusion and double porosity are not given. The current and proposed method of measuring hydraulic head using packer technology is considered inadequate. The NRC staff considers permanent (or semi-permanent) piezometers necessary to accurately evaluate hydraulic head (see Appendix G).

The tests planned for the test shaft and test facility are essential to the development of an understanding of the near-field hydrology, but do not in any

way remove the necessity for obtaining bulk hydrogeologic parameters for the far-field system.

In summary, the NRC staff includes that the proposed testing program will not yield the needed information on hydraulic parameters, aquifer/aquitard continuity and hydrogeologic effects of geologic discontinuities (See Appendices H and L).

Issue No. 1.1.1.2

1. Name of the Site: Hanford, Washington
2. Statement of the Issue: What is the method of data integration which is used to develop the three-dimensional distribution of hydrogeologic parameters?
3. Importance of the Issue to Repository Performance

The development of a continuous three-dimensional distribution of parameters from a finite number of measured data points requires a defensible method of data integration and interpretation.

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

60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

5. Summarize Pertinent Topics and the Summary of the Present State of Knowledge with an Analysis of Uncertainties

Present State of Knowledge

Available data (i.e., measured values of horizontal hydraulic conductivity) indicate that normal methods of interpretation between measured data are not valid because of very large and apparently unpredictable spatial variations. Existing performance models are based upon mean parameter values from single-hole tests which are considered representative of specific units. For example, the preliminary RHO performance model presented in the SCR (Section 12.4.3) subdivides the analysis domain into basalt flows consisting of dense zones and flow tops. With two exceptions, the hydraulic properties of each of the two types of layers (dense, flowtop) are the same.

Uncertainties

Large uncertainties will exist in interpretative methods because of large variations in measured values and lack of knowledge about their representativeness. It is not clear whether parameters spatially vary in a random manner or whether they vary in a definable manner.

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

It must be demonstrated that measured hydrogeologic parameters are representative at a scale appropriate for performance assessment. Also, an interpolative method to define the three-dimensional distribution of parameters must be developed and validated.

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

Hydrogeologic testing plans are discussed in 1.1.1.1. The detailed methodology by which measured data will be used to develop the three-dimensional distribution of hydrogeologic parameters is not presented in the SCR. The SCR contains a brief description of the use of geostatistical interpolation (Kriging) to analyze available horizontal hydraulic conductivity data from the Umtanum flow and Mabton interbed (pages 12.4-17 to 20). However, details of the analysis are not provided. The SCR indicates that results from testing activities will be continuously input to modeling studies and that "additional data needs will be established by an iterative process between data collection and modeling confidence" (page 13.3-47).

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

Interpolation of hydrogeologic parameters between points at which measured values exist is not feasible based upon existing data. If the variation currently reported (e.g., 4 to 6 orders of magnitude for horizontal hydraulic conductivity (BWIP, 1982c, p. 33)) is characteristic of repository scale volumes of material, then the methodology being used is appropriate. However, the methodology may be inadequate to achieve the required accuracy for performance evaluation. If parameter variation at a repository scale is much smaller than that observed in existing data, then an interpolative method could probably be developed and the required accuracy of performance evaluation may be achieved. It does not appear that the proposed program is sufficient in either case because of the limited number and locations of appropriate large-scale tests.

Issue No. 1.1.2

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What are the groundwater recharge and discharge locations, mechanisms, and amounts for the Pasco Basin?
3. Importance of the Issue to Repository Performance:

Knowledge of groundwater recharge and discharge locations, mechanisms, and amounts is necessary input for formulating both conceptual and mathematical models of groundwater flow systems in the Pasco Basin and for calculating travel times.

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

60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

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

Present State of Knowledge

Groundwater recharge and discharge locations for deep aquifers are currently not identified due to the complex distribution of hydraulic head data. Mechanisms and amounts of groundwater recharge and discharge are not defineable at this time. Data are conflicting but suggest that groundwater discharge enters the Columbia River within the Pasco Basin. DOE assumes that groundwater recharge areas are usually basalt outcrops while discharge is into either an overlying aquifer or into a surface water body (page 5.1-12). Thus, the major recharge area for the Grande Ronde would be outside the Pasco Basin at locations where the Grande Ronde is at or near surface. DOE assumes that the groundwater in the basalts discharges to the Columbia River near Wallula Gap (pages 5.1-57, 61, and 64). Assessment of the importance and magnitude of recharge/discharge through basalt confining layers is not possible because vertical hydraulic conductivity has not been measured.

Uncertainties

Groundwater recharge and discharge locations, mechanisms and amount in the Pasco Basin are not defineable at this time due to the complexity and limited areal distribution of the available hydraulic head data, limited data on vertical and horizontal hydraulic conductivity, and lack of demonstrated hydraulic continuity (Appendices G and L). Regional hydrochemical data which might help identify recharge and discharge locations and mechanisms have not been collected.

Water balance studies have proven inconclusive due to inaccuracies inherent in obtaining the required data. In particular, the large flow of the Columbia River makes it impractical to calculate potential discharge from deep basalts to the Columbia River based on measured river flows. That is, errors in flow measurement of the Columbia River exceed expected discharge from the basalt.

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

A broader data base is required in a vertical and areal sense that also minimizes the effects well drilling and testing procedures have on measured heads. Hydraulic head data are required that represent long-term water level recovery at most test intervals in all wells. Because variations will affect recharge/discharge mechanisms and amounts, vertical and horizontal hydraulic conductivity requires definition over broad areas in the vicinity of Reference Repository Location (RRL). Testing is needed on a number of colonnade/entablature zones to measure bulk values.

Detailed, accurate head and hydrochemical data delineating recharge/discharge areas are needed.

The impact of vertical leakage through what are assumed by RHO to be low hydraulic conductivity, confining layers must be assessed.

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

Evaluation of groundwater recharge/discharge will involve primarily continued field testing of hydraulic parameters and hydraulic heads within the Pasco Basin. In particular, vertical interaction between aquifers in the basalts as well as between basalt aquifers and unconfined aquifers will be evaluated using measurements of hydraulic head and vertical hydraulic conductivity. Hydrochemistry will also be used to evaluate vertical groundwater mixing. No additional regional recharge/discharge studies (i.e., outside the Pasco Basin) are discussed in the SCR. For purposes of modeling, emphasis will apparently be placed upon defining head and flux conditions at the boundaries of the Pasco Basin which constitutes the extent of the far-field model. Sensitivity studies will be conducted to evaluate the effects of different boundary conditions upon the modeled groundwater flow paths and travel times.

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

An evaluation of DOE's planned approaches is not feasible because no details are presented in the SCR. Details concerning dual- and multiple-borehole tests are not provided in the SCR, hence no evaluation can be made as to the likelihood of success in determining the previously described hydrogeologic parameters, especially vertical hydraulic conductivity. The concept of determining fixed point in time as well as time variant measurements of hydraulic heads is appropriate; however, details for obtaining time-variant measurements of hydraulic head are not presented. No evaluation can be made as to the probability of success in determining the variations in hydraulic head within the basalt intraflows and flow tops.

Staff believes that the importance of vertical leakage has not been sufficiently evaluated as a major recharge-discharge mechanism.

Issue No. 1.1.3

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What are the boundary conditions of the flow systems significant to repository performance?
3. Importance of the Issue to Repository Performance

Knowledge of boundary conditions is necessary input for formulating both conceptual and mathematical models of existing groundwater flow systems for analysis of repository performance.

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

60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

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

Present State of Knowledge

Boundary conditions of the Pasco Basin are basically unknown. External basin boundaries are no flux (flow) or constant flux and are controlled by geology and/or hydrology. Present knowledge only provides a general framework for the conceptualization of these boundaries. For example, past modeling efforts have based boundaries partially upon maps of the configuration of head distribution within the Mabton interbed (S.C.R., p. 12.4-7,15). Boundaries internal to the basin are also controlled by geology and/or hydrology. Examples include mapped and inferred structural and stratigraphic discontinuities (page 3.7-29 and Appendix L of this NUREG) and head pattern changes, such as flow toward Gable Mountain in the Mabton interbed (page 5.1-54).

Uncertainties

The existence and character of postulated boundaries are not definitive. The distribution of vertical and horizontal gradients in the basalts on the Hanford Reservation as well as near the Pasco Basin boundaries are poorly defined. Boundaries are postulated on the basis of structural features, not on the basis of head measurements and large scale, state-of-the-art pump tests. Boundary conditions must either be evaluated accurately or moved out far enough away from the region of interest (i.e., the Pasco Basin) that they do not significantly affect the model results.

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

Information about heads, permeabilities and mass fluxes at boundaries is required. It may be possible to obtain this information at least in part from calibration of Pasco-Basin-scale models. Model calibration is dependent upon

knowledge of the three-dimensional distribution of hydrogeologic parameters (see SIA 1.1.1).

Boundary conditions associated with structural or stratigraphic discontinuities must be identified by long-term, high-stress hydrogeologic testing. Lateral continuity of hydrogeologic properties requires definition, especially in the vicinity of the RRL. Definition of hydrogeologic significance of the Umtanum Ridge-Gable Mountain structural features north of the RRL is particularly important.

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

The SCR does not include a plan specifically directed toward boundary conditions.

Evaluation of boundary conditions will be based upon existing and future hydrogeologic data coupled with modeling studies. Since the planned hydrogeologic testing program concentrates on the RRL site and the Cold Creek Syncline, it is not apparent that data required for definition of boundaries will be obtained for the far-field modeling effort. Proposed tests for hydraulic parameters and heads in the areas of the far-field boundaries rely upon single-hole techniques.

Additional definition of the apparent hydrologic discontinuity west of the RRL will be achieved by the testing the McGee well and nearby boreholes (page 12.3-42).

Planned hydrogeologic data collection in the R.R.L. and the Cold Creek Syncline (Chapter 13) will be input to improve modeling and thus understanding of modeled boundary conditions.

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

It is important to define hydrogeologic boundaries with field data. The current hydrogeologic test plans place major emphasis upon the RRL site and the Cold Creek Syncline. It is not clear that the existing plans will be sufficient to define boundary conditions to the extent that a high degree of confidence can be placed on the results of far-field models. As an example, the potentially important Umtanum Ridge-Gable Mountain structural feature will not be investigated using multiple-hole tests under present plans. The reliance upon single-hole tests and head measurements using packer technology will probably not provide sufficient data to estimate heads and flux rates at far-field boundaries.

Issue No. 1.1.4

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: How and to what extent is groundwater flow affected by structural discontinuities?
3. Importance of the Issue to Repository Performance

Structural discontinuities can affect groundwater flow significantly. These structural discontinuities frequently are associated with hydrogeologic boundaries that are necessary inputs to the conceptual and mathematical models of groundwater flow systems for far field and Pasco Basin studies.

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

§ 60.21, 60.111, 60.112, 60.122, 60.123 & 60.124

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

The effect of structural discontinuities on groundwater flow is poorly understood. Little evidence exists indicating large scale structural discontinuities in the subsurface within the Cold Creek syncline area; however, geophysical and hydrological data indicate that numerous small-scale discontinuities may be present. Geologic and geophysical evidence are discussed in SIA No. 1.1.5 and Appendix L.

Little is known about the effects of structural discontinuities due to the limited understanding of the groundwater flow systems and related areal hydraulic continuity (Appendix H). Some of the hydrogeologic information collected to date has revealed evidence of the effects of structural discontinuities on the flow systems. Analysis of hydrochemical data presented in the SCR suggests that groundwater mixing is taking place in the vicinity of the Untanum-Gable mountain structure. Data from wells immediately west of the RRL indicate an abrupt change in a hydraulic head which may indicate the effects of a structural discontinuity. A northeast trending magnetic anomaly shown on Figure 3-52 of the SCR, is in the vicinity of this hydraulic head difference.

Uncertainties

Structural discontinuities have been inferred primarily from surface geophysical methods and little effort has been made to confirm and/or define their existence, nature and extent. Limitations in geological and geophysical methods allow for the possibility of undetected features (Appendix L and SIA No. 1.1.5). Considerable uncertainty regarding the nature of the groundwater flow systems exists, and the effect of structural discontinuities is highly dependent upon the conceptual groundwater model assumed. Discussion of the significance of conceptual groundwater models is presented in Appendix L.

Hydrologic testing has consisted of single-point borehole tests in small diameter holes which has done little to define the overall hydrologic system and assess the effects of structural discontinuities on the systems. Single-point tests stress the test horizon only within close proximity of the well so

results cannot be considered representative of the scale of structural discontinuities. Furthermore, the test hole locations (apparently) have not been controlled by inferred structural discontinuity locations shown on Figure 3-52 of the SCR, and few hydrologic data can be considered representative of structural discontinuities.

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

Further collection and interpretation of geologic and geophysical data are needed to accurately locate and identify structural discontinuities. The effects of known or inferred structural discontinuities on groundwater flow need to be defined together with location of any other discontinuities not detected by geological or geophysical studies. A much better understanding of the overall groundwater flow systems is essential to this goal. Testing is required on a scale large enough to stress a significant area; sufficient observation wells must be constructed to facilitate the location and definition of structural discontinuities. Such tests should be conducted on more than one interflow zone to verify the hydrogeologic continuity at the site.

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

Additional borehole investigation and prediction from tectonic models are planned. Boreholes designated for future testing include some in the Cold Creek Valley west of the RRL and DC-18 near the Gable Mountain structure. The nature of data expected from boreholes is not specified in the SCR, but presumably additional stratigraphic information and single-hole hydrologic test data will be obtained. Further analysis of large-scale structures, primarily through field mapping, is planned in an effort to refine the mechanical model to predict the nature and occurrence of structures. Numerical modeling of groundwater data will be done to define groundwater flow paths and predict effects of structural discontinuities.

8. Analysis of (7) as to Completeness, Practicality and Likelihood of Success

It is difficult to analyze the work plans because the SCR contains only general information on methods and location of further work. Drilling a few additional holes will provide additional stratigraphic information from which definition of some structural discontinuities may be possible. However, the location of proposed drilling sites does not appear to be determined by potential geophysical anomalies (Figure 3-52), so most of the inferred discontinuities will remain unconfirmed and others may remain undetected.

Knowledge of the groundwater flow systems and of the effects of structural discontinuities is very incomplete and proposed hydrologic testing will do little further understanding.

Other than the plans to test the Cold Creek Valley structure, no plans are presented to analyze the existence and significance of the inferred structures in the RRL area (Figure 3.52); therefore, these discontinuities will not be hydrogeologically characterized. Drilling and testing near Gable Mountain may increase the knowledge of ground water flow near this major structure but will

do little toward defining the existence and effects of structures on a large scale because multiple-hole, state of the art, pump tests apparently have not been planned in this area.

Large scale pump tests should not only better define hydrologic parameters but should also be useful in locating hydrogeologic boundaries which have not been detected by geologic or geophysical studies. Without studies directed specifically at structural discontinuities, the likelihood of defining the effects of structural discontinuities on groundwater flow to achieve realistic estimates of groundwater travel time is very low.

Issue No. 1.1.5

1. Name of the Site: Hanford, Washington
2. Statement of the Issue: How and to what extent is groundwater flow affected by stratigraphic and lithologic discontinuities?
3. Importance of the Issue to Repository Performance

Stratigraphic and lithologic discontinuities can significantly affect groundwater flow. These stratigraphic and lithologic discontinuities are associated frequently with hydrogeologic boundaries that are necessary inputs to the conceptual and mathematical models of groundwater flow systems and to travel time calculations.

4. Portions of 10 CFR 60 That Are Directly Connected to the Issue

60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

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

Present State of Knowledge

The Columbia River Basalt Group consists of numerous separate basalt flows varying in thickness and areal extent. The distribution of individual basalt flows within stratigraphic units containing multiple flows can be less continuous than the stratigraphic unit due to pinch out of individual flows. Internal flow structures vary markedly independent of flow distribution. Intraflow structures include variations of flow top, entablature, colonnade, vertical fans, vesicle zones, brecciation, and tiering. A relationship has been demonstrated between petrography and intra-flow structure such that flow top, colonnade and entablature can be identified. However, prediction of intraflow structure variation away from any sample location is unreliable. Some of the intraflow flow structures such as inverted fans could significantly increase fracture density and related vertical permeability. Fracture filling may moderate potential changes in vertical permeability. However, little is currently known about the extent, spacing and filling of fractures near the RRL (see Appendix L for further discussion).

Knowledge of the groundwater systems is so limited that the assessment of potential effects of stratigraphic and lithologic discontinuities is highly conjectural. Hydrologic testing to date has consisted of single-hole packer isolation tests which yield little data on bulk horizontal hydraulic conductivity and no data on vertical hydraulic conductivity. In addition, 95 percent of the tests have been performed on flow tops with the remaining five percent on flow interiors.

Uncertainties

A high degree of uncertainty exists with regard to the effect of stratigraphic and lithologic discontinuities on groundwater flow. This uncertainty is due to the severely limited understanding of the groundwater flow system, the

limited knowledge of the areal distribution of stratigraphic and lithologic discontinuities, and the inadequacy of the current testing program. The potential significance of stratigraphic and lithologic discontinuities on groundwater flow is highly dependent upon the degree of vertical interconnection assumed in the conceptual model which is used to describe the existing groundwater flow systems. Currently insufficient data exist to permit an accurate determination of the degree of vertical interconnection due to the potential effects of stratigraphic and lithologic discontinuities.

The SCR indicates that the location, nature, and distribution of stratigraphic and lithologic discontinuities cannot be predicted with any certainty. Thus, prediction of these effects through numerical modeling and related travel time calculations are very uncertain.

Single-well packer isolation tests are used to quantify horizontal parameters from vertically limited zones and do not provide vertical hydraulic conductivity data. Furthermore, single-well tests have a limited radius of investigation and cannot adequately test the scale of stratigraphic discontinuities. Certain intraflow structures (most significantly inverted fans) cannot be detected from fracture analysis in cores, petrographic analysis or borehole geophysical analysis. Therefore, these potentially significant features cannot be located or identified for testing.

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

Locations of lithologic or stratigraphic variation must be identified and state-of-the-art testing conducted at these locations to determine the effect of these discontinuities on groundwater flow and related travel times. Testing is required on a scale large enough to stress a significant area to include the scale of anticipated discontinuity. Sufficient observation wells to facilitate the general location and characteristics of discontinuities are needed. Identification of the type of discontinuity is not needed other than hydraulically. Tests should be conducted on more than one stratigraphic unit as well as individual flows to verify the overall hydrogeologic continuity at the site at various scales.

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

Additional testing is planned in both existing boreholes and a few new boreholes. The nature of the data expected from these boreholes is not specified in the SCR, but presumably will consist of additional stratigraphic information and 30 single-hole, four dual-hole and one cluster hydrologic tests. DOE plans to evaluate the significance of inverted fan structure on hydrogeologic properties only if such structure is identified during exploratory shaft construction. No information on how this evaluation might be done is presented in the SCR. Numerical modeling will be used to describe groundwater flow in zones of stratigraphic and lithologic variation.

8. Analysis of (7) as to Completeness, Practicality and Likelihood of Success

Additional drilling and borehole hydrologic testing may provide additional localized data, but large geographic areas will remain for which little or no data exist concerning stratigraphic discontinuities or groundwater flow system parameters. Construction of a numerical model will require the assumption of continuity among data locations. Therefore, the data base should demonstrate continuity. Current limitations in identifying heterogeneities from borehole data suggest that additional borehole data will not provide significantly greater resolution of subsurface stratigraphic and lithologic heterogeneities. In addition, single-hole hydrologic testing will yield little data useful to determination of hydrologic effects of these heterogeneities. The proposed program will be very incomplete, and the probability of such a program adequately defining the groundwater flow system will be very low without state-of-the-art, large-scale hydrologic testing oriented specifically toward stratigraphic heterogeneities.

Issue No. 1.1.6

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What is the hydrochemistry of the groundwater systems of the Pasco Basin?
3. Importance of the Issue to Repository Performance

Knowledge of hydrochemistry can be combined with other hydrogeologic data to better define both conceptual and mathematical models of existing ground water flow systems for farfield and Pasco basin studies. DOE hypothesizes that hydrochemical data can yield unambiguous information on the flow system at Hanford. Appropriate use of the hydrochemical data must be made in analyzing flow paths, flow rates and ages of groundwater.

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

60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

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

Present State of Knowledge

The SCR reports hydrochemical data from only 4 boreholes which penetrate the Grande Ronde. There has been no attempt to collect regularly spaced samples. While vertical hydrochemical profiles in some wells show apparent breaks in major ion, dissolved gas, and/or isotopic values, the profiles are not consistent among the four deep holes. Based on limited samples presented in the SCR and in the July 1982 hydrogeology workshop, the NRC staff notes that hydrochemical data from wells DC-12, DC-14 and DC-15 are compatible with a hypothesis of mixing between the Wanapum and Grande Ronde or even between the Saddle Mountains and Grande Ronde, as suggested by DOE for DC-15 (page 5.1-139). Carbon-14 analyses of inorganic carbon in the groundwater provide calculated model ages, but the model ages have not been corrected by state-of-the-art methods (Appendix F). Consequently, the NRC staff places no credence in the carbon-14 apparent ages reported in the SCR.

Uncertainties

The number of boreholes and the vertical spacing of data points within the boreholes is an inadequate data base for applying hydrochemical data to flow system analysis. DOE has presented no information in the SCR on methods and procedures of sampling and chemical analysis. Consequently, there is substantial uncertainty as to the validity and integrity of the analytical data. The potential for cross-unit mixing in open boreholes at BWIP has been raised by Witherspoon (1979), but the SCR does not address this uncertainty. The collection of water samples during the drill-and-test sequence described in the SCR (p. 5.1-14 - 5.1-15) is not a state-of-the-art sampling technique. Carbon-14 apparent ages have not been appropriately corrected for the effects of methane or other geochemical processes. DOE has presented no regional values of δD or $\delta^{18}O$ and no systematic paleoclimatologic and paleohydrologic

models with which their model of large scale recharge over geologically significant time spans can be tested. In the absence of such data and models, interpretations of stable isotopes of oxygen and hydrogen are highly uncertain. DOE has made no attempt to geochemically characterize methane from the Paleozoic section underlying the test basalts. Thus, their assertion that the methane in the Saddle Mountains and Wanapum Basalts was produced in-situ, rather than being produced in the Paleozoic section and concentrated in structural or stratigraphic traps in the younger basalts, has a measure of uncertainty. No measurements for matrix-diffusion coefficients in Hanford basalts have been presented in the SCR, nor have any estimates been used in preliminary assessments of matrix diffusion effects.

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

Representative groundwater samples must be acquired from locations and depths that are relevant to unit boundaries, the regional hydrologic system, and the proposed repository location for the hydrochemical and isotopic data to be applied appropriately. The boreholes used for sampling must be drilled in a manner that does not detract from sample integrity and be instrumented in a manner that provides for repeated sampling over long time periods. The data which are collected must be studied using state-of-the-art geologic, geochemical and isotopic conceptual and analytical models which are consistent with the overall conceptual model of groundwater flow.

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

DOE will continue to collect hydrochemical samples as part of the drill-and-test plan. Water samples will also be collected in the exploratory shaft and from newly drilled and existing boreholes. Additional stable and unstable isotopes will be evaluated for their potential for flow system characterization and age dating. Hydrochemical models are proposed for analysis of hydrochemical variations and evolution, although details of such models are not provided. A peer review of hydrochemical data is proposed to obtain a technical consensus on the nature of groundwater chemistry and its use in conceptual model development.

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

It is unreasonable to expect to obtain quantitative data on hydrochemistry and environmental isotopes that can be used to conclusively describe the origin, flow paths and age of the groundwater at depth in the Pasco Basin. While hydrochemical and isotopic data can provide useful supportive information, primary evaluation of the flow system must be based on hydrogeologic information and on the results of large-scale hydraulic testing and accurate measurements of hydraulic head.

In the opinion of the staff, hydrochemistry should be used as supporting data in the evaluation of hydrostratigraphic units and groundwater flow systems, not as the primary data. DOE is placing much significance upon hydrochemical indications of distinct, separate flow systems and low vertical hydraulic

conductivities. We believe the flow system should be evaluated using standard hydrogeological testing techniques (e.g., large-scale pump testing) and that hydrochemistry should be used to support the results of physical testing. Alternatively, it must be demonstrated that hydrochemistry can be used for quantitative evaluations of groundwater flow.

Issue No. 1.1.7

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What is the conceptual groundwater flow model?
3. Importance of the Issue to Repository Performance

Conceptual models of the hydrologic system guide development of numerical models used to predict groundwater flow and travel times and dictate the location, type and extent of future testing.

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

§ 60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

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

Present State of Knowledge

The preliminary conceptual hydrogeologic model is a stratified sequence of permeable flow tops separated by nearly impermeable flow interiors resulting in a highly confined flow system(s). Flow is assumed to be essentially lateral and controlled by the attitude of basalt units. Recharge to and discharge from deep basalt units is assumed to occur only where these units are at or near the surface or where vertical discontinuities permit significant vertical movement. Significant vertical mixing is thought to occur only where vertically disruptive features exist.

Uncertainties

The major uncertainty is whether the proposed conceptual model is valid. The variability and uncertainty in existing hydrogeologic data permit the formulation of several alternate conceptual models including:

- o Continuous layered, leaky confined system (relatively high vertical hydraulic conductivity areally)
- o Large-scale homogeneous system with discontinuous layers (anisotropic)
- o Structurally controlled semi-isolated cells (bounded by low hydraulic conductivity structures or zones)
- o Structurally controlled, conduit-dominated system (bounded by high hydraulic conductivity structures or zones)

Other uncertainties in the conceptual model result from uncertainties in hydraulic parameters, hydraulic heads and hydrogeologic boundaries (e.g. structural and stratigraphic discontinuities, recharge/discharge) as outlined in Issues 1.1.1 through 1.1.6.

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

Alternative conceptual models need to be considered that fit the existing data (see Appendix L). Representative bulk values for hydraulic parameters and reliable long-term hydraulic heads must be determined. Hydrogeologic boundaries must be located and assessed. The conceptual models should be reassessed based upon these new data. It may be possible to reduce the number of alternative conceptual models, even more alternative conceptual models may be required.

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

The planned efforts to refine the existing conceptual model are based on the additional determination of hydraulic properties, hydraulic heads, and hydro-chemistry from existing and new boreholes. These efforts are based primarily on single-borehole tests and limited multiple-borehole tests. Results from test activities will be input to mathematical models to identify additional data needed to refine the conceptual model.

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

The NRC staff finds that the existing hydrogeologic data could support several conceptual hydrogeologic models and not just the preliminary hydrogeologic model proposed by the DOE. Other conceptual models are certainly possible given the large variation and uncertainties in existing data. However, the SCR does not consider alternative conceptual models, nor do the plans specify that such a consideration will be made in the future. The hydrogeologic test plans are not considered adequate to definitively evaluate all possible conceptual models. Representative bulk values of hydraulic parameters, long-term hydraulic heads and evaluation of hydrogeologic boundaries are considered extremely important by the NRC staff, if a definitive conceptual model is to be determined. The tests proposed by DOE are considered inadequate for obtaining the required data (see Issues 1.1.1 to 1.1.6).

The groundwater flow system(s) in Hanford basalts would appear to be amenable to large-scale testing (Appendix E). Such testing would not only yield bulk hydraulic parameters and information on hydrogeologic boundaries, but may verify the conceptual model(s) most appropriate to the Hanford basalts.

Issue No. 1.1.8

1. Name of the Site: BWIP - Hanford, Washington
2. Statement of the Issue: What are the mathematical models used to predict groundwater flow?
3. Importance of the Issue to Repository Performance

A mathematical model to predict groundwater travel times and flow paths is essential to predictions of repository performance.

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

§ 60.21, 60.111, 60.112, 60.122, 60.123 and 60.124

5. Present State of Knowledge With an Analysis of Uncertainties

Present State of Knowledge

DOE has obtained or formulated a number of numerical codes for near-field and far-field groundwater modeling. The level of sophistication of the numerical codes is high. The conceptual groundwater model used by DOE (see issue 1.1.7) consists of horizontal, laterally continuous basalt layers with permeable flow tops and interbeds and low permeability dense flow interiors. DOE's numerical models have been based only upon this conceptual model, including the most recent effort present in the SCR, utilizing the code PORFLO (pages 12.4-28 to 50). This latest model utilizes simplified geology, constant parameter values within layers and assumed boundary conditions. It is not clear from the SCR that existing models have been calibrated against measured head conditions.

Uncertainties

Major uncertainties are associated with all existing numerical groundwater flow models of the Pasco Basin and near-field. The most significant uncertainty is in the validity of the conceptual model (see SIA 1.1.7). Other uncertainties result from the highly variable nature of hydraulic parameters, unknown boundary conditions, the lack of appropriate hydraulic head data to use for model calibration, and the failure to include specific geologic conditions. Uncertainties associated with the mathematical bases of the numerical models are relatively low but not insignificant.

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

Alternative conceptual models which fit existing data need to be developed. Measurements of representative bulk hydraulic parameters and reliable long-term hydraulic heads are required. Hydrogeologic boundaries must be located and assessed. Based upon the additional information, conceptual models should be assessed and numerical models developed for all valid conceptual models. Calibration of numerical models based upon representative hydraulic

heads is required. Additional calibration could be made against large-scale hydrogeologic tests.

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

The present conceptual groundwater flow model will be refined by additional determinations of hydraulic properties, hydraulic heads and hydrochemistry from existing and new boreholes. Existing numerical codes will be verified and bench marked. Selected models will be used to predict groundwater travel times and flow paths. Parametric and sensitivity studies will be conducted to identify key parameters, parameter distributions and model inputs. Stochastic models may be used to bound predictive uncertainty. Numerical groundwater models will also be used to guide additional needs for field investigations.

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

The NRC staff finds that the proposed plans for mathematical modeling are not adequate to predict groundwater flow system behavior. Apparently the DOE will consider only the existing conceptual flow system model as a basis for mathematical models. Existing data indicate that other conceptual models may be possible (see issue 1.1.7), and therefore should be considered by mathematical modeling or conclusively disproven.

The NRC staff is concerned that the proposed field program is not adequate to provide representative hydraulic parameters, hydraulic heads and hydrogeologic boundary conditions as noted in issue 1.1.1 to 1.1.6. In particular, the lack of representative long-term hydraulic heads will not allow sufficient calibration of numerical models. Furthermore, DOE does not demonstrate how consideration will be given in numerical models to the interactions between the shallow unconfined aquifers and the deep basalt. This is important because of the significant water table changes which have occurred at the RRL site as a result of artificial recharge activities. No plans are presented for the calibration of numerical models against large-scale tests, even though such calibration would add considerable validity to the numerical models.

DOE has taken the approach of testing components of the hydrogeologic system and then using numerical models to combine components and predict the hydraulic behavior of the system. One advantage of the Hanford site is its testability using large-scale hydrogeologic tests (Appendix E). Therefore, it is possible to directly observe the hydraulic behavior of the system, rather than rely totally upon predicted hydraulic behavior from numerical models.

REFERENCES

1. BWIP, "Test Plan for Obtaining Geotechnical Data Acquiring Usage of Boreholes to Support Site Characterization for a Nuclear Waste Repository in Basalt," Rockwell Hanford Operations, RHO-BW-PL-1-P, 1982a.
2. BWIP, "An Assessment of Geologic Data Needs Acquiring Borehole Drilling and Testing to Support Site Characterization Activities for a Nuclear Waste Repository in Basalt," Rockwell Hanford Operations, RHO-BW-EU-2-P, 1982b.
3. BWIP, "An Assessment of Hydrologic Data Needs Requiring Borehole Drilling and Testing to Support Site Characterization Activities for a Nuclear Waste Repository in Basalt, RHO-BW-EU-3-P, 1982c.
4. Domenico P., R. A. Freeze, S. P. Neuman, F. L. Parker, F. J. Pearson, H. Tanaka, I. Remson, H. Ross, D. Ford, D. Swanson, W. Tenhofel, and staff of the Basalt Waste Isolation Project, "Hydrology and Geology Overview Committee Reports and Responses from the Basalt Waste Isolation Project," Rockwell Hanford Operations, RHO-BWI-LA-50, 1981.
5. Neuman, S. P., and P. A. Witherspoon, "Field Determination of the Hydraulic Properties of Leaky Multiple Aquifer Systems," Water Resources Research, 8, (5), 1284-1298, 1972.

APPENDIX L

**STRUCTURAL AND STRATIGRAPHIC CHARACTERISTICS RELATED TO
GROUNDWATER FLOW AT THE HANFORD SITE, WASHINGTON**

01/28/83

BWIP DSCA/APP L/LOGSDON

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EXECUTIVE SUMMARY

Current geologic studies conducted by the Rockwell Hanford Operations Energy Systems Group for the Department of Energy (DOE) on the Hanford Site are reviewed in this appendix as part of an effort to evaluate the potential of basalt as a high-level radioactive waste repository site. The analysis reflects the NRC staff's evaluation of techniques used and results obtained in studies of stratigraphy and structural relationships as related to hydrogeology within the Pasco Basin. Which are cited in the SCR

Major stratigraphic (geologic) subdivisions consist of the Columbia River Basalt Group and suprabasalt sediments. Suprabasalt sediments vary significantly in thickness and can include sediments of the Ringold Formation, the Hanford Formation and surficial deposits. All sedimentary deposits exhibit considerable facies variation. Stratigraphic units are defined on gross lithology obtained through analysis of surface exposures and borehole samples. Paleomagnetism has proved of little use in further subdivision of sedimentary units.

Principal techniques for definition of basalt stratigraphic units include major-element and trace-element chemistry, paleomagnetism, including variation in polarity and inclination angle, and borehole geophysics. Basalt chemistry is the most widely used technique but needs additional stratigraphic control to be most effective, particularly in the Grande Ronde Formation. Problems encountered with the techniques include: (1) little chemical or magnetic polarity variation within flow groups, (2) large statistical variation of inclination angles within a sampled unit, and (3) variation of physical parameters that affect geophysical log responses.

Stratigraphic investigation of the basalts has produced delineation and lateral correlation of individual members and chemical subtypes within the three major subdivisions of Grande Ronde, Wanapum and Saddle Mountains basalt. Definition and correlation of units within the Saddle Mountains and upper Wanapum is more complete than for the Grande Ronde because a greater number of unique chemical types and polarity reversals occur in the two formations. Intraflow structure variation of selected Grande Ronde flows was examined and a correlation between flow petrography and intraflow structure has been recognized. Prediction of lateral intraflow structure variation is difficult and essentially lacking. This has potentially major implications with respect to groundwater flow.

The primary technique for the evaluation of structure is synthesis of surface geophysical data with stratigraphic information to produce structure contour maps and display geophysical anomalies. Assumptions made in contour map construction, while necessary because of limited available data, could affect interpretations. Strain analysis and mechanical modeling of major Yakima-type folds in the area also have contributed to structural interpretation.

Geologic mapping indicates the Cold Creek syncline to be an asymmetric feature with variation in axial direction and plunge. Little evidence exists to support major structural discontinuities within the Cold Creek syncline, although the presence of numerous geophysical anomalies indicates that

small-scale features may be present in the subsurface. Again, these features may be very important with respect to determining flow path and travel time from the repository.

The geologic studies have been effective in defining stratigraphy and major structures within the Cold Creek syncline area. Substantial uncertainty still exists concerning definition and continuity of flows within the lower Wanapum and parts of the Grande Ronde basalts and the presence of small-scale structures in the area. Questions of potentially greater significance exist with respect to the effect of stratigraphic and structural variation on the various hydrogeologic parameters important to repository performance. Geologic mapping of stratigraphic units has correlated basalt formations successfully on the basis of rock chemistry, paleomagnetic data, and interbed definition by boreholes. Little work has been done toward converting these geologic stratigraphic units to hydrostratigraphic units that can be demonstrated to be continuous or discontinuous with defensible assigned values of saturated hydraulic conductivity, thickness, porosity, and storage coefficient. The conceptual groundwater flow model presented in the SCR is based on an assumption of a stratified hydrologic system. Hydrologic and geologic data indicate that a variety of alternative conceptual models are equally plausible. Some information exists to indicate that the basic assumption of stratification of the flow systems may not be valid. Efforts to conduct long-term, large scale state-of-the-art tests (Hantush, 1960; Neuman and Witherspoon, 1972) would prove useful in eliminating uncertainties.

1 INTRODUCTION

This appendix presents an evaluation of methodology and current results of continuing Basalt Waste Isolation Project (BWIP) geology studies and their implications with respect to groundwater hydrology within the Pasco Basin in south-central Washington State. This report is part of an evaluation of a program to determine the feasibility of underground high-level radioactive waste storage in the layered basalt sequence of the Columbia River Basalt Group. Studies on which this report is based are centered currently on an area known as the Cold Creek syncline area within the Hanford Site. Figure 1 shows the area under investigation and illustrates the location of major geographic features of the Pasco Basin and Hanford Site. Most of the references listed herein are products of the BWIP research effort.

The purpose of this report is to serve as a reference for analysis of groundwater flow issues which are part of the NRC review of the "Site Characterization Report for the Basalt Waste Isolation Project" (SCR). The general objective is to assess the approaches taken in defining the area's geology and to ascertain the completeness and reliability of these geologic studies with respect to understanding the controls on groundwater flow. Specific objectives are as follows: (1) present information on techniques used in the assessment of stratigraphy and a discussion of the resulting conclusions, (2) present the same information and discussion of structure and (3) evaluate the effects of the uncertainties in geologic information on the conceptual model of groundwater flow presented in the SCR. On less otherwise stated information concerning the BWIP geologic studies summarized in this appendix has been gathered from two major reports prepared by the BWIP geologic staff (Myers and others, 1979; Myers and Price, 1981) and the SCR.

2 STRATIGRAPHY

Evaluation of a potential site for a repository requires a detailed understanding of stratigraphy in the vicinity of the proposed location. Such an understanding is essential to determining the continuity of individual stratigraphic units, the nature of geologic structures and related tectonic deformation, and the thickness and extent of hydrostratigraphic units. Knowledge of stratigraphic discontinuities is particularly important in evaluating potential paths and travel times for radionuclide movement, both vertically and horizontally to the accessible environment.

Within this section, discussion centers on two major stratigraphic subdivisions: the basalts and interbedded sediments of the Columbia River Group, and the group of sediments which overlie the basalts. Discussion of each subdivision involves evaluation of the techniques used to define stratigraphic units and analysis of the results of these techniques in determining the stratigraphic framework. Figure 2 presents the stratigraphic sequence and nomenclature presently recognized within the Pasco Basin.

2.1 Suprabasalt Sediments

The suprabasalt sediments are a complex group of deposits which include stream, flood and lacustrine facies as well as assorted facies of volcanic

and near-source erosional origin. The sedimentary deposits range in thickness from 0 to greater than 200 m (meters) (0-660 feet). They embrace a complex history of changing facies complicated by periods of erosion and/or nondeposition. Although the sediments are not under consideration as a repository host rock, their stratigraphy and age have considerable importance in defining the structural evolution of the Pasco Basin.

2.1.1 Techniques

Definition of stratigraphic units within the suprabasalt sediments has depended primarily upon investigation of surface exposures, borehole cuttings and core. Delineation of stratigraphic units is based primarily on differences in lithology and/or texture. Generally, techniques involve the measuring and sampling of surface stratigraphic sections and analysis of borehole samples to detect facies variations. Subsurface information collected is mainly in the form of cuttings from cable tool or rotary borings; however, a number of coreholes have been drilled specifically to obtain corroborating data on the suprabasalt sediments. In addition, Tallman and others (1981) reported the use of granulometric analyses and calcium carbonate determinations on samples from selected boreholes to assist stratigraphic delineation and correlation.

Definition of stratigraphic units on the basis of lithologic and textural variation is desirable because it provides a direct means of unit identification. It also has limitations, particularly in sediments that exhibit considerable facies variation. While definition of gross lithologic units seems quite possible within the suprabasalt sediments, definition and correlation of lithologic variation within these gross units are less likely. In addition, rotary or cable tool drilling techniques produce disaggregated samples which may be adequate for interpretation of gross lithologies but may introduce considerable error into efforts to recognize more subtle lithologic changes.

To a lesser extent geophysical methods have been used to help determine unit thickness and distribution. Surface geophysical methods, including gravity and magnetics, have helped to define the top of underlying basalt and the total thickness of the sediment sequence. Surface techniques have not been particularly useful in determining position and thickness of individual units, however.

Borehole geophysical data have been obtained from selected drill holes. These data have assisted in defining major stratigraphic units as well as facies changes within the units. Borehole geophysical methods can be of considerable use within sequences similar to that of the suprabasalt sediments. Often units which have some lithologic variation will produce a consistent geophysical signature in response to consistent porosity, density or natural radioactivity. These same features necessitate, however, that identification and correlation based on borehole geophysics must be carefully controlled by lithologic data. In addition, in an area where contamination by human induced radioactivity is a possibility, reliability of results from induced and natural radiation tools is less certain.

Analysis of remnant magnetic polarity of sedimentary units has been done also in an attempt to further define stratigraphic relationships within the suprabasalt sediments. Packer and Johnston (1979) report analytical results of

nearly 300 samples from both surface and subsurface locations. Their work on surface exposures indicates the possibility of definition and correlation of three polarity changes within the upper Ringold unit. Unfortunately, within the Cold Creek syncline, only a very thin upper Ringold unit is present which significantly reduces the possibility of surface to subsurface correlation. Furthermore, the coarse conglomeratic nature of the middle Ringold unit does not facilitate determination of paleomagnetic polarity data and analysis is restricted to a few thin sequences of fine material distributed throughout this unit. Thus, the absence of the upper Ringold and the difficulty in obtaining reliable data from the middle unit renders the use of paleomagnetism in defining stratigraphic units or time horizons difficult. Despite this fact, Tallman and others (1981, p. 2-3) report that paleomagnetic data are being used to delineate time-stratigraphic units; however, no discussion of such units is presented. It is unlikely that paleomagnetism will be of great significance in further defining stratigraphic units unless data of a greater consistency can be obtained.

2.1.2 General Stratigraphy

The complex nature and relationship of facies within the suprabasalt sediments has resulted in description of a variety of sedimentary units. Currently, three major divisions of the sedimentary sequence are recognized. These divisions are the Ringold Formation, a sequence informally referred to as the Hanford Formation, and the overlying recent accumulations collectively referred to as surficial deposits.

Suprabasalt sediments within the vicinity of the Cold Creek syncline consist mainly of the Ringold Formation and the Pasco Gravels of the Hanford Formation. Tallman and others (1981, p. 2-13) report Ringold sediments in the area of the Reference Repository Location (Figure 1) to be predominantly of type I ("normal" Ringold sequence) but note that interfingering of type III (fanglomerate deposits) sediments occurs in the area's western part. Parts of the four principal units (basal, lower, middle, upper) within the type I sequence are recognized, but their occurrence does not remain consistent throughout the entire area. In some areas, principally the synclinal flanks, erosion and/or non-deposition have resulted in the absence of either part or all of some of the units.

The Hanford Formation is primarily a sequence of Pasco Gravels within much of the Cold Creek syncline. Myers and others (1979, p. 2-24) report excellent exposure of these gravels in excavations for waste facilities east of the Reference Repository Location. Distribution of the Hanford Formation within the Cold Creek syncline area is highly variable. It thins and thickens in response to glacial-floodwater paths and subsequent erosion.

Developing an understanding of the nature and stratigraphic relationship of suprabasalt sediments is a difficult task. The sediments are of considerable importance because they provide a key to unraveling much of the tectonic history of the Pasco Basin. Unfortunately the nature of the units themselves and the method of deposition makes confident delineation and correlation of units difficult. In addition, analysis of variations in thickness and/or depositional history is complicated by channel cutting and erosion which,

when coupled with a necessarily limited sample inherent in subsurface correlation, can lead to confusion and/or incorrect analysis.

2.2 Basalt

Although suprabasalt sediments are important as indicators of recent geologic history, the thick sequence of flood basalts which underlie the sediments is of even greater significance. Precise knowledge of thickness, extent and internal character of individual basalt flows is imperative because the basalts are the proposed repository host rock. Stratigraphic discontinuities may provide the avenues for rapid vertical movement of contaminants from the repository horizon to the accessible environment. Thus, considerable effort has been directed toward defining unit stratigraphy of the Columbia River Basalt Group within the Pasco Basin.

2.2.1 Techniques

A variety of techniques has been employed to define and trace numerous basalt flows present in the basin. These techniques include determination of major- and trace-element chemistry of basalt flows, examination of mineralogical and textural variation, analysis of fracture and intraflow structures, determination of natural remanent magnetism and geophysical studies. Principal methods of stratigraphic identification and correlation (chemical analysis, paleomagnetism, geophysics) are discussed in separate sections. Discussion of mineralogical and textural variation and their relationship to intraflow structure are presented in the section on Grande Ronde Basalt.

2.2.1.1 Chemical Analysis

Mineralogic and petrographic similarity among many of the basalt flows has necessitated developing other methods of differentiating individual flows or flow groups. Chemistry, particularly major-element chemistry, has become the dominant criteria upon which stratigraphic division of the Columbia River Basalt Group is based. Although chemical analyses of basalts have been conducted for some time, little significant use was made of this technique in defining stratigraphy until Waters (1961) delineated three chemical variations in the basalts of the Columbia River Group. In the following decade significant progress was made in relating major-element chemistry to stratigraphy, ultimately leading to the establishment of a series of chemical types (Wright and others, 1973) which provide unique identification of individual flows or flow groups. Continued field mapping and related analysis of major-element chemistry resulted in the establishment of a formal stratigraphic nomenclature for the Columbia River Basalt Group (Swanson and others, 1979a). This formal stratigraphy is based almost entirely upon major-element chemical types.

Subsequent to the codification of stratigraphical nomenclature, additional definition of units has occurred in and around the Pasco Basin (Myers and others, 1979; Myers and Price, 1981). Units within the Pasco Basin and much of the Columbia Plateau have been divided into three major formations based primarily on chemical type. These formations are, in order of decreasing age, the Grande Ronde, the Wanapum and the Saddle Mountains basalts (Figure 2). Individual members within these formational units have also been described.

Members within the Saddle Mountains Basalt are usually represented by a single chemically unique flow, while members within the Wanapum include multiple flows. No member designations within the Grande Ronde have as yet been formalized. The dearth of member designations within the Grande Ronde is due to a lack of chemical diversity among the numerous basalt flows which make up 80% of the three formation's combined volume.

The inability to define units within the Grande Ronde with desired precision using major-element chemistry has precipitated attempts to use trace-element chemistry to achieve more desirable results. Early attempts using trace-element data to define stratigraphy were performed by ARHCO (1976). Trace-element data were used with major-element chemical data to delineate basalt units in and around the Pasco Basin. McDougall (1976) also used trace-element data to differentiate flows and flow groups in a variety of locations throughout the Columbia Plateau. Reidel (1978) showed that discriminant analysis of major- and trace-element data could further refine correlation, and later Reidel and Long (1980) applied these techniques to basalts in the Pasco Basin.

Work by Reidel (1978) and Long and others (1980) indicates the most useful chemical constituents for flow identification appear to be a combination of selected major and trace elements. MgO, TiO₂, Zr, Ba, and P₂O₅ were found to be most useful for discriminant analyses of Grande Ronde Basalt chemistries (Reidel and Long 1980).

While chemical analysis is the single most important tool in defining basalt stratigraphy, it is not without limitations. Virtually every flow within younger basalt sequences, most notably the Saddle Mountains Basalt, is a unique chemical type. This uniqueness permits accurate identification of each flow at differing locations. Chemical composition within the Grande Ronde and, to a lesser extent the Wanapum basalts, often does not change significantly between adjacent flows or among a group of several basalt flows. Reidel (1978, p. 127), recognizing the limitations of total reliance on chemistry, noted that basalt chemistry is not adequate for flow correlation and that physical characteristics and stratigraphic position are equally important factors. He also noted (p. 137) that if stratigraphic control is added, evaluation capabilities improve. Discussion of specific limitations with respect to stratigraphy of the Pasco Basin is addressed subsequently in a discussion of stratigraphy.

2.2.1.2 Paleomagnetism

Determination of the natural remanent magnetism of individual basalt flows is one of the techniques being used in an attempt to delineate stratigraphy of basalt units. Early work by Watkins (1965) and Rietman (1966) indicated that reversals in magnetic polarity occur within the thick sequence of the Columbia River Basalt Group. This work indicated also that such reversals might be useful as a tool for stratigraphic correlation. Regional work by Swanson and Wright (1976) led to subdivision of the basalt sequences by polarity intervals. These intervals were later included in the description of formal stratigraphic units by Swanson and others (1979a). Choiniere and Swanson (1979) used secular variation of the geomagnetic field to correlate flows of the Columbia River Basalt Group with similar flows from the Oregon coast. They determined that virtual geomagnetic pole positions of these flows were unique enough to permit tentative correlation.

Work in the Pasco Basin (Myers and others, 1979) resulted in recognition of many of the regional polarity intervals both in surface and subsurface samples (Figure 2). Unfortunately, polarity intervals within the thick Grande Ronde sequence include many flow groups; consequently division on the basis of polarity alone did little to assist definition of flow stratigraphy. Subsequent efforts investigated the possibility of using other criteria such as changes in inclination angle, secular variation and magnetic intensity to further break out individual units.

Initial attempts by Coe and others (1978) to determine paleointensity of some Grande Ronde flows exposed near Sentinel Gap (Figure 1) were largely unsuccessful. However their work, and that by Packer and Petty (1979), indicated that variation in inclination angle from flows within the same polarity interval is evident, and that correlation between surface and subsurface locations using inclination angle variation is possible. Some Grande Ronde flows exhibited consistently unique paleomagnetic inclination angles which permitted correlation with reasonable certainty. Others, however, lacked clear-cut distinction thereby making correlation much less certain.

Long and Landon (1981) report recent, although as yet unreleased, work of stratigraphic delineation based upon secular variation of paleomagnetic direction. They present no comparison of secular-variation units to stratigraphic ones; however, they do indicate that, at present, correlation of the secular-variation units is limited. Although information is limited, a figure referenced in the discussion by Long and Landon (1981) indicates that the units are based only on variation of inclination angle rather than true secular variation, which includes changes in declination. This distinction may be little more than academic, however, as Coe and others (1978, p. 19) point out that for the Grande Ronde flows sampled at Sentinel Gap, most variation in paleomagnetic direction is in the inclination component.

Work by Packer and Petty (1979) indicates that, in general, samples collected from surface sections yielded results of good stability. Samples tested from core, however, were less consistent. In their evaluation several samples were collected and analyzed from individual flows. A mean and standard deviation was calculated for each group. In some cases groups had a narrow standard deviation while in other cases the variation was large. Part of this variation may have resulted from the fact that selection of sample group was based upon other stratigraphic factors such as common chemical type or geophysical log response.

Thus, while sample groups had similar chemistry, large standard deviation of inclination data may indicate that selection of group boundaries were in error. This error would inadvertently force a stratigraphic configuration on the data group. Packer and Petty also indicate that the large variation in inclination data could be caused by a variety of factors including remagnetization by an overlying flow, chemical alteration, remagnetization by the drilling process, or related core handling problems.

A variety of alternatives may affect the results of paleomagnetic inclination data; this substantially influences the degree of certainty of stratigraphic delineation by this method. Such a method is likely to be useful only when

good repeatability of magnetic data is present and when it is supported by other methods.

2.2.1.3 -Geophysics

Surface geophysical techniques used have included seismic, magnetic, gravity, and electrical methods. With the exception of seismic techniques, the surface geophysical methods have been employed largely to define the top of the basalt surface and the nature and magnitude of subsurface structures. Attempts were made to obtain and laterally trace seismic-reflections from individual flows or flow groups but they generally were unsuccessful. The seismic-reflection study indicated little velocity contrast to be present between basalt flows; individual flows or flow groups seldom returned consistent reflections. Thus, seismic-reflection techniques, while potentially useful for defining the basalt surface and near surface structures, provide little assistance in defining and tracing subsurface stratigraphic units. In contrast to surface methods, borehole geophysical techniques have proved useful in defining and tracing stratigraphic units. They are particularly useful in obtaining stratigraphic data in boreholes from which samples or core were not taken. Siems and others (1974) demonstrated the potential for borehole geophysics in combination with major-element chemistry as a stratigraphic tool. Later work by Brown (1979) showed that borehole geophysics could be used reliably for subsurface correlation over substantial areas. Myers and others (1979) report being able to trace a flow within the upper part of the Grande Ronde on the basis of its consistent borehole geophysical response.

The principal disadvantage of borehole geophysical technology is that the instrumentation responds primarily to changes in physical parameters of the flow and, to a lesser extent, to some changes in major-element chemistry. Thus, identification and correlation of flows can be difficult and misleading because a flow will undergo sufficient change in physical character to alter its geophysical response from one location to another. Correlation using borehole geophysics alone is difficult because of these problems and because borehole conditions can affect log responses profoundly. Nevertheless borehole geophysics is a useful tool in subsurface stratigraphic definition and correlation when it is combined with other stratigraphic methods such as flow chemistry and paleomagnetism.

2.2.2 General Stratigraphy

The current understanding of stratigraphic relationships of the Columbia River Basalt Group within the Pasco Basin is based primarily on rock chemistry, paleomagnetism and geophysics. Physical examination of drill cores is used for examination of intraflow structures. Much of this discussion is directed toward stratigraphy of the Grande Ronde Basalt because stratigraphy of the Wanapum and Grande Ronde basalts is less well defined than that of the Saddle Mountains Basalt, and because current interest in a waste-storage horizon is directed at units within the Grande Ronde. The discussion is also directed to the area known as the Cold Creek syncline because this is the area in which potential locations for a storage site are being investigated. Basic stratigraphic relationships and unit nomenclature are presented in Figure 2.

2.2.2.1 Grande Ronde Basalt

Definition and correlation of individual flows within the thick Grande Ronde sequence are difficult because of their chemical and paleomagnetic homogeneity. Regional work by Swanson and others (1979a) indicated a consistent change in potassium and magnesium chemistry within the total Grande Ronde sequence; the delineation of two subdivisions informally recognized as the high-magnesium (high-Mg) and low magnesium (low-Mg) sequences resulted. This chemical change within the Pasco Basin has been recognized and the names Sentinel Bluffs for the upper high-Mg sequence, and Schwana for the underlying low-Mg sequence have been applied (Myers and others, 1979). Swanson and others (1979a) also recognized a very-high-Mg chemical type in the Grande Ronde which has also been found in the Pasco Basin. Long and others (1980) delineated chemical subtypes for flows in the immediate area of the Schwana-Sentinel Bluffs contact. In addition, they report the presence of thin flows or parts of flows separated stratigraphically from the Umtanum flow (Figure 2) with chemistry characteristic of the Umtanum subtype. They also note the presence of less extensive flows of low-Mg chemistry within the basal part of the high-Mg Sentinel Bluffs sequence and flows of very-high-Mg chemistry within the upper part of the low-Mg Schwana sequence. Myers and others (1979) have suggested five chemical subtypes for the part of the Schwana sequence below the Umtanum flow, however, insufficient data exist to determine whether or not these subtypes are really extensive.

The Sentinel Bluffs sequence is considerably thinner than the Schwana sequence and identification and correlation of flows is somewhat easier. Long and others (1980) delineated a chemical subtype for the McCoy Canyon flow which is, in most locations, the lowermost unit within the Sentinel Bluffs sequence. They delineate this subtype in comparing it with chemistry of flows stratigraphically adjacent to it. When compared with the entire high-Mg sequence, the McCoy Canyon flow is much less distinct. Trace element chemistry also appears to be useful in defining units within the Sentinel Bluffs sequence. Long and Landon (1981) report changes in chromium content appear to define at least one individual flow and a flow group within the Sentinel Bluffs.

While the stratigraphic relationship of these various chemical subtypes is understood generally, the above discussion indicates some of the potential problems in relying on chemical types for identification and correlation of Grande Ronde basalt flows. Additional definition of chemical subtypes probably will depend to an even greater degree on subtle distinctions among adjacent flows. Thus the usefulness of these chemical differences will depend upon an increasing knowledge of stratigraphic relationships.

Paleomagnetism also helps identify stratigraphic horizons within the Grande Ronde. Swanson and others (1979a) report four basic polarity intervals (R1, N1, R2, N2) for the Grande Ronde sequence (Figure 2). Only the R2 and N2 polarity intervals have been encountered within the Grande Ronde sequence investigated in the Pasco Basin. R1 and N1 intervals presumably exist but at depths as yet unexplored. Long and Landon (1981) report that secular-variation units within these polarity intervals have been recognized and are being used for correlation purposes. While some individual basalt units may possess significantly unique magnetic parameters (e.g., inclination angle or

secular variation) that permit their identification, samples collected from other units often exhibit a wide variation in parameter values. Furthermore, changes in some paleomagnetic parameters may occur only between large groups of flows. Such inconsistencies in data can limit the reliability of paleomagnetism for stratigraphic purposes.

Considerable work has been done also in evaluating intraflow structure within the Grande Ronde sequence. Long (1978) investigated several flows of the Sentinel Bluffs sequence both in surface section and in drill core. His investigation included an evaluation of types of intraflow structures present and a comparison of these types with flow petrography. On the basis of this work, Long proposed that these Grande Ronde flows exhibit three general types of intraflow structure. The types are based primarily on entablature, flow top and colonnade development within the flows. Subsequent examination of flows from other locations indicated that while representatives of each type are present, "intraflow structure types are best thought of as end members with nearly continuous gradations between all of the types" (Long and Davidson, 1981, p. 5-10).

Analysis of fracture logging from cores proved of little use in identifying these intraflow structures; however, petrographic analyses of both surface and core samples appear to show a relationship between petrography and intraflow structure. Although mineralogical and textural characteristics of Columbia River Basalts are similar enough to preclude use of these characteristics in flow identification, Long (1978) noted changes in glass abundance and texture between entablature and colonnade within individual basalt flows. The consistency of these changes, regardless of the flow being observed, led to a conclusion that, within individual basalt flows, entablature and colonnade could be distinguished on the basis of these petrographic differences. This relationship between petrography and intraflow structure is significant because it appears to provide a means of determining intraflow structure within the subsurface.

Despite the apparent ability to delineate entablature and colonnade within the subsurface, the nature of lateral intraflow variation is more difficult to assess. Long and Davidson (1981) report that the Umtanum flow may change completely from one intraflow structural type to another between surface exposures. They also report (p. 5-32) that fanning column structures within Umtanum surface exposures radiated from "centers spaced at intervals ranging from a few to 160 m" (530 ft). According to the SCR (p. 3.5-25) "...the intraflow structures may vary greatly in thickness, be absent entirely from any given flow, or occur repeatedly within a single flow."

Comparison of Grande Ronde intraflow structures among coreholes reveals considerable variation in intraflow structures within the Cold Creek syncline area. The SCR (p. 3.5-32) concludes that

"The location of other features, (in intraflow structures) such as thinning of colonnade, multiple tiers of entablature or colonnade, fanning of entablature columns, and thickening of flow-top breccia probably cannot be predicted with any certainty. These features should, however, be anticipated in the Umtanum and other Grande Ronde flows..."

Knowledge of intraflow structures is critical because of the potential effect that they may have on groundwater movement. Such features have a low probability of being identified in the subsurface by analysis of cores but have a high probability of being important hydrologically. Their existence and hydrologic significance is best understood based upon results of large scale pump testing.

2.2.2.2 Wanapum Basalt

The Wanapum Basalt is comprised of the Frenchman Springs, the Roza and the Priest Rapids members, all of which are present within the Basco Basin. These members have a combined thickness in excess of 400 m (1320 ft) in the southern portion of the basin and thin to between 300 and 400 m (990-1320 ft) within the Cold Creek syncline area. The Frenchman Springs Member makes up between 190 and 220 m (630-720 ft) of the total Wanapum (Reidel and Fecht, 1981). Efforts to identify and correlate Frenchman Springs flows have been of limited success. Reidel and Fecht (1981) report no obvious chemical differences among flows, and paleomagnetic data also are not definitive. They report (p. 3-11) seven to nine flows or flow lobes to be present in the Frenchman Springs Member within the Cold Creek syncline area; however, their individual correlation across the area is currently not possible because of similarities between flows.

The Roza Member consists of one or two flows or flow lobes; it averages about 50 m (165 ft) in thickness; however, within the Cold Creek syncline, its thickness approaches 70 m (230 ft). The Roza is not identifiable by chemical means because of chemical similarity between the Roza and Frenchman Springs members. It is, however, one of the few flows within the entire Columbia River Group that is distinguishable in hand specimen because of its even phenocryst distribution. The Roza also has a transitional paleomagnetic direction which helps distinguish it from the normal polarity flows of the Frenchman Springs Member.

Flows of the Priest Rapids Member overlie the Roza. Swanson and others (1979a) report two distinct chemical types (Lolo and Rosalia) within the Priest Rapids; both are present in the Pasco Basin. Reidel and Fecht (1981) report that generally only one flow of each chemical type is present; however, multiple flows or flow lobes of the Rosalia type are present in some areas. Within the Cold Creek syncline, only two flows have been recognized with total thickness varying from 40 to 70 m (130-230 ft) (Reidel and Fecht, p. 3-13).

2.2.2.3 Saddle Mountains Basalt

Distribution of individual Saddle Mountain Basalt units within the Pasco Basin appears much less uniform than units of the Wanapum Basalt. Units of the Saddle Mountains Basalt are usually recognized more easily and subsurface correlation is much more certain than is the case for the Grande Ronde and Lower Wanapum basalts. Saddle Mountains flows are characterized by individual chemical types and distinct paleomagnetic polarities and by the development of interbedded sediments between basalt flows. These characteristics coupled with the closer proximity of the Saddle Mountains Basalt to the surface have allowed a much more complete understanding of flow distribution from

core/drill hole data for the Saddle Mountains than for either the Wanapum or Grande Ronde basalts. Details on characteristics of individual flows or flow units of the Saddle Mountains Basalt are presented in the SCR and earlier BWIP publications. They are not discussed in this report because of the much greater importance of stratigraphic features of the Grande Ronde and Wanapum Basalts to repository related groundwater flow patterns.

2.2.2.4 Interbasalt Sediments

Interbedded sedimentary deposits of the Ellenburg Formation are present within the Columbia River Basalt Group particularly between members of the Saddle Mountains Basalt. The interbeds vary in distribution and thickness and contain a variety of facies. Most interbeds contain tuffaceous sand, silt and clays and occasionally exhibit coarser facies. The sediments are generally poorly indurated but do contain layers of welded tuff or similar lithified material.

In most locations, the three basalt formations are separated from each other by sedimentary interbed. The Vantage interbed occurs between the Grande Ronde and Wanapum basalts while the more extensive Mabton interbed is present between many of the Saddle Mountains basalts. Sedimentary interbeds occur between many of the Saddle Mountains members and to a lesser extent members of the Wanapum Basalt. No interbeds are present within the Grande Ronde Basalt.

Thickness and distribution of these sedimentary units are highly variable being dependent upon the mode of deposition and pre-depositional topography. The Mabton interbed appears to be most extensive and reaches a thickness in excess of 45m (150 ft.) in the Cold Creek syncline area. Most interbeds are less extensive with thickness of these units commonly lesser than 20m (65 ft.).

2.2.2.5 Discussion

Significant progress has been made in defining subsurface stratigraphy within the Pasco Basin and the Cold Creek syncline area despite the similar chemistry and magnetic polarity of many of the flows. Delineation of valid chemical types and subtypes along with more refined paleomagnetic techniques have resulted in definition and correlation of many individual basalt flows with a high degree of certainty.

Although the stratigraphic framework appears consistent, discontinuities which are of significance for waste storage considerations are poorly understood. Discontinuities such as flow pinch outs could have a significant impact on groundwater movement and related contaminant travel time. Discussion and figures presented in the SCR (p. 3.5-18; Fig. 3-23,24) for example indicate that the number of basalt flows within the Sentinel Bluffs sequence varies from 6 to 10. This variation indicates that numerous stratigraphic discontinuities associated with flow distribution are likely present within the Cold Creek syncline area. Techniques for further definition of intraflow structures are limited to additional drilling or hydrologic testing. Even with additional core holes, data are obtained only a relatively small sampling of a particular flow; few assumptions can be stated reliably about the extent of intraflow conditions apparent in the cores. It is possible that large-scale hydrologic testing might provide additional information on

variation of basalt flow characteristics in the subsurface. Hydrologic testing considerations are discussed in more detail later in this report.

3 STRUCTURE

As mentioned in the introduction, evaluation of geologic studies of the Cold Creek syncline requires investigation of two topics: structure and stratigraphy. Evaluation of structural deformation within the Pasco Basin and the Cold Creek syncline requires a discussion of the techniques and methods used to define structures and of completeness of resulting structural interpretation.

3.1 Techniques.

Myers (1981, p. 8-1) lists four methods of field investigation that were integrated in efforts to define subsurface structures within the Cold Creek syncline area. The four methods are: (1) surface geologic mapping of bedrock, (2) borehold geologic studies, (3) structural analysis of Yakima folds, and (4) geophysical surveys.

An understanding of stratigraphy is an essential part of investigating structural deformation in any location. Consequently, some of the methods for definition of structural features, including field mapping and some borehold studies and geophysical techniques, were employed in stratigraphic definition within the Pasco Basin. They are mentioned here only briefly because earlier discussions of stratigraphy included evaluation of these techniques. Discussion of techniques presented here center on principal surface geophysical methods used and on efforts to analyze Yakima folds in the area.

3.1.1 Surface and Borehold Geologic Studies

Surface geologic mapping and borehold geologic studies were combined to produce a series of structure contour maps. These maps were prepared for several surfaces including the top of basalt, top of the Wanapum Basalt, top of Grande Ronde Basalt, and the top of the Umtanum flow within the Grande Ronde. These surface maps are the basis for most of the conclusions concerning subsurface structure in the Cold Creek syncline.

The number of drill hole data points in the older surfaces is significantly less than for the top of basalt because of the depth of older basalts. In fact, Myers (1981) reports that data from about 300 holes were used in defining top of basalt, whereas data from some 25 holes were available to define the top of the Wanapum, and even fewer were available for the top of the Grande Ronde. Many of the borehold geologic studies involved the collection of lithologic and stratigraphic data; these data were discussed previously. Some borehole studies were conducted specifically to obtain data on subsurface deformation and related stress evaluation. These methods, reported by Moak (1981), include analysis of core to determine the presence and nature of tectonic breccia and evaluation of a phenomena known as core diskings.

Evaluation of breccia included examination of core and geophysical logs for zones of brecciation and determination of the cause of brecciation. Moak

(1981) lists intervals from 15 boreholes that were examined for tectonic breccia and related features. Some of these zones exhibited tectonic features while others did not. Generally, there appears to be a limited amount of tectonic brecciation within the area investigated. In most cases the brecciation is interpreted as representative of small-scale features. Moak (1981, p. 6-3) does report, however, that most of the tectonic breccias identified, are in the Grande Ronde and Wanapum basalts.

Core diskings, the tendency for core to separate into a series of thin disks, also was investigated. This diskings phenomenon is of interest because it occurs in core from the Umtanum and other Grande Ronde flows. Moak (1981, p. 6-8) reports that no definitive relationship between drilling method or flow petrology and the diskings phenomena could be established. Currently, it is thought that diskings is a result of higher horizontal than vertical stresses within a basalt flow.

3.1.2 Analysis of Yakima Folds

Work on definition of Yakima folds consists primarily of studies by Price (1981) on the Umtanum Ridge structure. Price developed conclusions about strain geometry and, ultimately, a mechanical model to explain the formation of the Umtanum Ridge structure through a program of detailed mapping and evaluation of strain features. Other structures were examined briefly to see if they showed features similar to those of Umtanum Ridge and whether or not their formation could be explained with the same model. Price concluded that at least two other locations exhibit structural relationships similar to that of Umtanum Ridge. Price concluded also that since the Cold Creek syncline is in close proximity to the eastern extension of the Umtanum Ridge structure, the mechanism for the development of the Umtanum structure is the same as that which produced the Cold Creek syncline. The model proposed by Price suggests that relatively little strain is present in synclinal troughs and, hence, resulting deformation is small. Boreholes studies mentioned above indicate that some faulting is present within the syncline. The SCR (p. 3.7-17) reports that "Small fault zones a few centimeters to 1 meter in apparent width have been observed in cores taken from many core holes (Moak, 1981a). Gouge and fractures associated with these small faults physically resemble those observed within anticlines...Any moderately dipping basalt may contain similar small, disseminated low-dip faults."

3.1.3 Surface Geophysics

An extensive program of surface geophysical investigation also was used in evaluating structure. Major surveys were conducted using aeromagnetic and seismic methods; gravity and, to a much lesser extent, electrical methods were used to facilitate interpretation in selected areas.

3.1.3.1 Seismic Investigations

Most early seismic investigations in basalt utilized only refraction methods. In some cases such surveys were useful in differentiating basalt from overlying sediments, but little success was achieved in delineating individual basalt flows. Holmes and Mitchell (1981) report that early (1963) refraction studies in the Pasco Basin encountered problems with velocity inversions

which made interpretation difficult, and that reflection studies were limited by shothole expense and the lack of digital recording techniques. However, seismic reflection is now considered to be a useful technique for tracing subsurface units because of recent advances in seismic energy sources and seismic-reflection data processing. An extensive seismic-reflection survey was undertaken over much of the Cold Creek syncline area. Holmes and Mitchell (1981) report that in excess of 200 km (124 miles) of reflection lines were run over a two-year period.

Processing of seismic-reflection data involved the same procedures used in petroleum exploration. Processing included stacking and trace-enhancement techniques. It was hoped that such a survey would produce consistent traceable reflections from deep reflectors such as flows within the Wanapum or Grande Ronde basalts, but little consistency in reflection data was apparent below the top of basalt. Holmes and Mitchell (1981, p. 8-8) report that modification in both collection and processing techniques were subsequently implemented in an attempt to define more shallow reflecting horizons such as the top of basalt and units within the Saddle Mountains Basalt. Results presented by Holmes and Mitchell indicate that this was successful in some areas of the survey. Other profiles however, show few consistent reflecting horizons. On the basis of these seismic data, a series of seismic anomalies were defined and targeted for further investigation. The SCR presents the general categories of these anomalies on figure 3-33 (p. 3.6-4). A program for quantitative assessment of the seismic reflection data is described in chapter 13 of the SCR.

3.1.3.2 Magnetics

Discussion presented by Swanson and others (1979b) of an early low-level aeromagnetic survey flown over part of the Columbia Plateau indicates the potential of this method for defining structures and other features within the Columbia River Basalt Group. As a result a high-sensitivity aeromagnetic survey was flown over the Pasco Basin in early 1980 (Holmes and Mitchell, 1981). Five constant elevation surveys between 760 and 1680 m (2500-5500 ft) were flown as part of this survey. Data were assembled in the form of contour maps; in addition, Werner deconvolution profiles were run along each flight line. The profiles were used in identifying anomalies which could be significant structurally. Like the seismic anomalies, magnetic anomalies were then plotted on a map of Cold Creek syncline area and efforts were made to determine their nature and significance. Some of the apparent seismic and magnetic anomalies were examined in greater detail. Detailed evaluation involved use of other techniques such as ground magnetic and gravity profiling; in a few cases, electrical resistivity measurements were implemented. Development of a general structural picture of the Cold Creek syncline area involved interpretation of structure contour maps produced by combining surface and subsurface geologic and geophysical data. In addition, data obtained from evaluation of borehole tectonic features were included where appropriate. In some cases structure contour and geophysical anomalies revealed good correspondence. In other cases, anomalies and basalt surface data appeared inconsistent.

3.1.4 Results

Results of the synthesis presented by Myers (1981) indicate the Cold Creek syncline is a rather broad asymmetric feature with a steeply dipping limb to the southwest. The syncline is bounded by large scale structures such as the anticlinal features associated with Umtanum Ridge-Gable mountain on the northeast and Rattlesnake Hills-Yakima Ridge to the south. The synclinal axis trends generally northwest-southeast but alters to a near east-west trend in some locations (Figure 3). In addition, the structure appears to change plunge direction which suggests changes in its attitude normal to the axial strike in some locations. Structure contour maps and geophysical anomalies indicate the presence of numerous small-scale structural changes within the syncline, some parallel to synclinal strike and others of a cross-cutting nature (Figure 4). Figure 4 is a reproduction of Figure 3-52, page 3.7-29 of the SCR. While none of these structures appears to be a major disruption of general structural trends, many are not well defined and at present little is known about the presence, nature, extent and potential effects of these features on groundwater flow. As an example, Myers (1981) notes a feature in the northwest end of the syncline which, based on magnetic anomalies, appears to cross-cut synclinal strike. Although magnetic data indicate the presence of such an anomaly, little reinforcement of it is apparent from seismic-reflection data and structure contour maps do not define its existence clearly. Therefore, whether a cross-cutting structure does in fact exist is not at all certain. What is known is that hydraulic head data from water wells west of this general area appear to be about 70 m (225 feet) higher than those obtained to the east (SCR, p. 5.1-55). Thus, numerous questions exist as to the presence of structures in the subsurface, whether these structures are reflected in geophysical surveys, and what effect, if any, these structures might have on groundwater flow.

Several assumptions were made in the process of structural evaluation of the Cold Creek synclinal area. These assumptions, although possibly justifiable by the nature and distribution of data, could have affected conclusions significantly. Myers (1981) points out that in preparation of structure contour maps, primary emphasis was placed on defining the top of the basalt and that interpretation of structure is based largely upon this particular contoured surface. However, such a map is not a true structure contour map because the top of basalt is not necessarily a consistent stratigraphic horizon. Consequently, changes in elevation interpreted as structure may in fact be erosional elevation changes in the basalt; some structures may show little surface expression. Myers (1981, p. 8-11) indicates that where chemical data were available, attempts were made to distinguish erosional from structural control; however, significant parts of the top of basalt map are based on surface geophysical data where this distinction is not possible.

Preparation of structure contour maps of horizons beneath the top of basalt was accomplished largely by subtracting contoured isopach data from the top of basalt map. Consequently, except where specific control points exist, structure contour maps are at least in part a projection of the top of basalt surface. Although this procedure may be necessary because of lack of adequate control on deep horizons, it may introduce considerable error; there is no guarantee that structures at depth will necessarily be reflected in a contour map of the top of basalt surface.

It is doubtful that these assumptions have either created or masked any stratigraphically disruptive structures of major proportion. Indeed, evaluation of current stratigraphic and structural information suggests the presence of a structural feature creating a vertical stratigraphic disruption of major proportion within the Cold Creek syncline is unlikely.

However, the number, location and nature of small scale features are poorly known. While these features may not produce significant stratigraphic disruption, their effects upon groundwater flow and the related integrity of a waste repository are highly uncertain.

4 HYDROGEOLOGIC IMPLICATIONS

4.1 Introduction

The vertical and horizontal distribution of hydrogeologic properties is of major importance to the feasibility of underground high-level radioactive waste storage in the basalt sequence of the Columbia River Basalt Group. Distribution of hydrogeologic properties in the Grande Ronde and Wanapum basalts units is dependent upon the structural and stratigraphic features described in this report. This section is a discussion of the significance of structural and stratigraphic discontinuities on groundwater flow. The discussion of their significance is presented in light of different conceptualizations of basalt groundwater flow. A brief section on current hydrologic testing in the Cold Creek syncline area follows the evaluation of stratigraphic and structural discontinuities.

4.2 Stratigraphic and Structural Discontinuities

The primary difficulty in assessing the hydrologic implications of stratigraphic and structural discontinuities at the Hanford site is a very limited understanding of the nature of groundwater flow in basalts. This problem is highlighted in several portions of the RHO overview committee report (Demenico et al., 1981). It is difficult to predict the effect of subsurface geologic changes on groundwater flow because, to date, little is known about the way groundwater moves through a fractured medium like basalt. Until recently it has been assumed that the presence of high permeability interflow zones and low permeability flow interiors within a layered sequence of basalt flows produces a stratified groundwater flow system. The dense, presumably low permeability, flow interiors are assumed to be effective aquitards that limit vertical movement of groundwater and result in dominantly horizontal movement within each layered zone.

A conceptual groundwater flow model of the Cold Creek syncline has been proposed in the SCR and can be described as an areally continuous, layered system with minimal vertical leakage. Because of the relatively impermeable nature attributed to individual basalt flow interiors, recharge to and discharge from subsurface basalt units are assumed to occur only where these units are present at or near the surface or where significant structural discontinuities such as major anticlines or faults permit vertical interconnection. Based upon these assumptions, the model produced in the SCR indicates recharge is taking place only along topographically prominent ridges such as Umtanum and Yakima Ridge with flow to the south and east through the Cold Creek Syncline. No avenue for

vertical leakage is assumed to exist because no large-scale structures are present within the syncline. Thus, while discharge from the Saddle Mountains Basalt is thought to occur at locations where the units are in close proximity to the Columbia River, discharge from the Wanapum and Grande Ronde basalts is believed to occur only at the south end of the Pasco Basin near Wallula Gap where a large fault and/or near surface location of these units permits vertical movement.

Results of stratigraphic and structural studies presented earlier indicate that other equally viable conceptual models can be proposed. Such models include but are not limited to:

1. An areally continuous, layered system with high vertical leakage. In this conceptual model, the intraflow structures, such as inverted fans or hackly entablature development, are considered to permit significant vertical leakage between layers and reduced but not eliminate totally the assumed confining nature of basalt flow interiors. In all respects this is a porous-flow-equivalent, continuum model like that of the DOE.
2. An areally discontinuous, layered system with high vertical leakage that performs hydraulically as a large-scale, homogeneous, anisotropic system. In this conceptual model, the layered basalt system is laterally discontinuous because of intraflow structures (e.g., page 3.5-25) and variable flow distribution (e.g., page 3-18, 3.-22, 23 and discussion of those figures). These small-scale discontinuities would result in a homogeneous system on a large-scale due to their high frequency of occurrence and random distribution. Furthermore, the high vertical leakage associated with intraflow structures would impart an anisotropy to this model system. This is also a porous-flow-equivalent, continuum model.
3. An areally discontinuous, layered system bounded by high permeability structures. In this conceptual model, the layered basalt system is divided into a series of discrete blocks as suggested by SCR Figure 3-52 (page 3.7-29). The blocks are bounded by vertically disruptive features of high permeability (e.g., fault zones or tectonic breccias) which provide a direct means of recharge and discharge to and from deep aquifers. On the scale of the zone between the RRL and the accessible environment, this is a non-continuum model for which the porous-flow equivalent numerical modeling used in the SCR could yield erroneous and non-conservative flow paths, travel times, and radionuclide fluxes.
4. An areally discontinuous, layered system bounded by low permeability structures. In this conceptual model, the layered basalt system is divided into a series of discrete blocks separated by low permeability zones which impede lateral groundwater movement. The low permeability barriers might consist of gouge zones along major faults or might represent simple juxtaposition of low horizontal hydraulic conductivity units (e.g., a dense basalt flow interior) against high horizontal hydraulic conductivity units (e.g., a brecciated flow top). As with case 3 above, this is a non-continuum model, though in this case containment of radionuclides might be exceptionally good, depending on the vertical leakage within a given block.

The importance of stratigraphic or structural changes in the lateral continuity of individual basalt flows on groundwater flow becomes immediately evident if flow is assumed to conform to the conceptualized stratigraphy. Any feature which disrupts lateral hydraulic continuity will presumably interrupt normal horizontal groundwater flow. A discontinuity like a fault or a fractured fold axis could create a barrier to groundwater flow or provide a conduit for vertical movement of groundwater (Newcomb, 1961) not feasible under normal layered conditions. The presence of a direct vertical conduit among otherwise stratified zones could create discharge conditions for some zones and recharge conditions for others, and significantly disrupt horizontal groundwater flow. A vertical conduit could also "short circuit" normal flow paths and travel times of radioactive contaminants resulting in their premature and unpredicted release to the accessible environment. The presence of significant changes in basalt intraflow structure would also result in groundwater flow paths and travel times significantly different than those predicted by a stratified groundwater flow model. Intraflow structures such as inverted fans or hackly entablature development could significantly increase the vertical leakage between layers and reduce the assumed confining nature of basalt flows to vertical migration of contaminants.

Recent work by Brown (1980) has indicated that the concept of a stratified groundwater system may not be totally valid. Comparison of hydrostatic head data with stratigraphy from a variety of locations within the Columbia Plateau reveals that head changes expected as a result of stratigraphic isolation of aquifers do not occur. Instead, thick basalt sequences containing several laterally extensive basalt flows exhibit very little vertical change in hydrostatic head. Significant changes are found to occur across zones of sedimentary interbed material. These results produced a conclusion that structural and stratigraphic discontinuities within basalt flows permit a much higher degree of vertical groundwater flow than thought previously, and that sedimentary interbeds are more important than basalt flows in limiting vertical groundwater movement. Hydrochemical data in Hanford wells DC-6, DC-14 and DC-15 suggest that the Vantage interbed may function in this manner at those locations.

If such a non-stratified concept is valid, then the potential effects of stratigraphic and structural discontinuities are an inherent aspect of groundwater flow conceptualization. The disappearance of a particular basalt flow, for example, could mean the connection of two otherwise unconnected hydrologic zones in the stratified model; however, if vertical interconnection already exists among basalt flows, the pinching out of one unit would have a minimal effect on hydrostatic head and related groundwater flow. Similarly, small-scale structures which might vertically disrupt a stratified anisotropic system are less significant in a more isotropic unstratified system.

Flow in the Cold Creek syncline could be significantly different than that proposed in the SCR if a nonstratified conceptualization is valid. The prospect of significant vertical leakage among basalt flows indicates that recharge to and discharge from deep aquifers could be taking place in much closer proximity to a repository horizon than in a stratified system.

Each of the above conceptual models is as likely an explanation of groundwater flow as that proposed in the SCR. Currently the amount and reliability of hydro-

logic data collected are limited such that it is virtually impossible to eliminate any of these models. Clearly, depending upon the model chosen to explain the collected data, groundwater flow and related contaminant travel time could be interpreted as either highly beneficial or highly detrimental to repository performance.

The conceptual model of groundwater flow in the vicinity of the Reference Repository Location as presented in the SCR is based upon horizontal layers of high and low hydraulic conductivity - a stratified groundwater system. As such, structural and stratigraphic discontinuities are especially important. The SCR descriptions of geology (Chapter 3) and hydrogeology (Chapter 5) indicate that structural and stratigraphic discontinuities are present within the Cold Creek Syncline. However, the study program has not provided an assessment of their location and characteristics nor their hydrologic importance. The problem is summarized in the following three statements.

1. Significant structural and stratigraphic discontinuities have not been fully identified using geologic and geophysical studies. Little is known about small scale features such as intraflow structures, flow boundaries, tectonic fractures and tectonic breccia zones. Presently, there are probably many undetected features. The predictability of such features is poor if not impossible. The brief discussion presented above suggests that indications of structural and stratigraphic discontinuities are present; they are not seen as significant enough in the SCR to warrant detailed investigation.
2. Geologic and geophysical studies are limited in their abilities to characterize adequately the complex nature of structural and stratigraphic discontinuities in the basalts of the Pasco Basin. Therefore, it is expected that features important to groundwater flow will remain poorly understood even after the planned geologic and geophysical studies outlined in Chapter 13 of the SCR are completed.
3. The structural and stratigraphic discontinuities that have been identified to date have not been adequately tested hydrogeologically at the scale of the features. No large scale state-of-the-art pump tests have been conducted to obtain bulk values of either vertical or horizontal hydraulic conductivity. The problem has been highlighted in several portions of the RHO overview committee report (Domenico, et al., 1981).

Consideration of potential effects of specific structural and stratigraphic features on groundwater flow within the Pasco Basin yields an important conclusion. This conclusion is that a basic understanding of how groundwater behaves in a layered basalt sequence is lacking. This creates a fundamental problem in evaluating the progress of current research and in producing an accurate and realistic assessment of the effects of particular conditions on the groundwater flow system. Consideration of some of the possible conceptual models above reveals significant differences on the effects of stratigraphic and structural discontinuities. Resolution of these differences cannot be achieved until basic questions of how the basalt hydrologic system operates are answered. Of even greater importance is the ability to assess repository performance without a basic understanding of the hydrologic system.

4.3 Hydrologic Testing Program

The hydrologic testing program that has been followed in the Cold Creek syncline-area appears to have accomplished little in defining the groundwater flow system. The program has involved predominantly single hole, drill stem-packer type tests which produces information on hydrostatic head and hydraulic conductivity for selected thin zones within each borehole. The conductivity values obtained appear to be of little use in defining hydrostratigraphic units or in determining the effect of structural or stratigraphic discontinuities. There appears to be little consistent correlation of these values among boreholes. While a higher density of boreholes might provide additional information, it is unlikely that increased collection of these data will improve significantly the reliability of the data and understanding of the system. Significant questions will continue to exist concerning the applicability of the point values obtained from single hole testing as being representative of the hydrologic system.

The pump testing program outlined in Chapter 13 includes single, dual and cluster borehole testing (see SCR p. 13.3-39 and 41). The SCR testing program is not sufficiently explained to judge the extent to which structural and stratigraphic discontinuities will be identified and examined hydrologically. Large-scale pump testing (affecting an area of 3-5 km² (1.8-3 mi²) is needed to help define subsurface discontinuities and provide an examination of hydrologic continuity within the Cold Creek syncline. Without this scale of testing, it is not possible to achieve the level of understanding necessary for mathematical modeling under the framework of hydrostratigraphic units. It is doubtful that any holes other than cluster 16a, b and c can be tested adequately.

5 CONCLUSIONS

1. Significant structural and stratigraphic discontinuities have not been fully identified using geologic and geophysical studies. Little is known about small-scale features such as intraflow structures, flow boundaries, tectonic fractures and tectonic breccia zones. Presently, there are probably many undetected features. The predictability of such features is poor if, not impossible.
2. Geologic and geophysical studies are limited in their abilities to characterize adequately the complex nature of structural and stratigraphic discontinuities in the basalts of the Pasco Basin. Therefore, it is expected that even after the planned geologic and geophysical studies outlined in Chapter 13 of the SCR, features important to groundwater flow will remain poorly understood.
3. The structural and stratigraphic discontinuities that have been identified to date have not been adequately tested hydrogeologically at the scale of the features. No large-scale state-of-the-art pump tests have been conducted to obtain bulk values of either vertical or horizontal hydraulic conductivity, or to detect discontinuities.
4. A sufficient number of structural and stratigraphic discontinuities may be presented within the Cold Creek syncline area to modify or invalidate the basic

conceptual model of stratified groundwater flow in basalts presented in the SCR. Consideration should be given to alternative conceptual models because the conceptual model in turn directs future data collection and modeling efforts.

5. The pump-testing program outlined in Chapter 13 of the SCR may not provide a large enough scale to examine or detect structural and stratigraphic discontinuities. Testing of hydrologic continuity is necessary for mathematical modeling based upon the framework of hydrostratigraphic units.

REFERENCES CITED

- ARCHO, 1976, Preliminary feasibility study on storage of radioactive waste in Columbia River Basalts: ARH-ST-137, Atlantic Richfield Hanford Company, Richland, Washington.
- Brown, J. C., 1980, Stratigraphy and groundwater hydrology of selected areas, Columbia Plateau, Washington: Washington State University, College of Engineering Research Rept. 80/15-39, 20 p.
- Brown, J. C., 1979, Investigation of stratigraphy and ground-water hydrology, Columbia River Basalt Group, Washington: Washington State University, College of Engineering Research Rept. 79/15-37, 61 p.
- Brown, R. E., 1975, Groundwater and the basalts in the Pasco Basin: in Proceedings of the Thirteenth Engineering Geology and Soils Engineering Symposium, April 2, 3, 4, 1975, Moscow, Idaho.
- Coe, R. S., Bogue, S., and Myers, C. W., 1978, Paleomagnetism of the Grande Ronde (Lower Yakima) Basalt exposed at Sentinel Gap: potential use for stratigraphic correlation: RHO-BWI-ST-2, Rockwell Hanford Operations, Richland, Washington.
- Choiniere, S. R., and Swanson, D. A., 1979, Magnetostratigraphy and correlation of Miocene basalts of the northern Oregon coast and Columbia Plateau, southeast Washington: American Journal of Science, v. 279, no. 7, p. 755-777.
- Domenico, P. R. A. Freeze, S. P. Neuman, F. L. Parker, F. J. Person, H. Tanaka, I. Remson, H. Ross, D. Ford, D. Swanson, W. Twenhofel, and Staff of the Basalt Waste Isolation Project, "Hydrology and Geology Overview Committee Reports and Responses from the Basalt Waste Isolation Project," Rockwell Hanford Operations, RHO-BWI-LD-50, 1981.
- Flint, R. F., 1938, Origin of the Cheney-Palouse scabland tract: Geological Society of America Bulletin, v. 49, p. 461.
- Gephart, R. E., Arnett, R. C., Baca, R. G., Leonhart, L. S., and Spane, F. A. Jr., 1979, Hydrologic studies within the Columbia Plateau, Washington: an integration of current knowledge: RHO-BWI-ST-5, Rockwell Hanford Operations, Richland, Washington.
- Hantush, M.S., 1960, Modification of the theory of leaky aquifers; Journal of Geophysical Research, vol. 65, no. 11, p. 3713-3726.
- Holmes, G. E., and Mitchell, T. H., 1981, Seismic-reflection and multi-level aeromagnetic surveys in the Cold Creek syncline area, Appendix B, in Myers, C. W., and Price, S. M., editors, Subsurface geology of the Cold Creek syncline: RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.
- Long, P. E., 1978, Characterization and recognition of intraflow structures, Grande Ronde Basalt: RHO-BWI-LD-10, Rockwell Hanford Operations, Richland, Washington.

Long, P. E., Ledgerwood, R. K., Myers, C. W., Reidel, S. P., Landon, R. D., and Hooper P. R., 1980, Chemical stratigraphy of Grande Ronde Basalt, Pasco Basin, south-central Washington: RHO-BWI-SA-32, Rockwell Hanford Operations, Richland, Washington.

Long, P. E., and Landon, R. D., 1981, Stratigraphy of the Grande Ronde Basalt, in Myers, C. W., and Price, S. M., editors, Subsurface geology of the Cold Creek syncline: RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Long, P. E. and Davidson, N. J., 1981, Lithology of the Grande Ronde Basalt with emphasis on the Umtanum and McCoy Canyon flows, in Myers, C. W., and Price, S. M., editors, Subsurface geology of the Cold Creek syncline: RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

McDougall, I., 1976, Geochemistry and origin of basalt of the Columbia River Group, Oregon and Washington: Geological Society of America Bulletin, v. 87, p. 777-792.

Moak, D. J., 1981, Borehole geologic studies, in Myers, C. W., and Price, S. M., editors, Subsurface geology of the Cold Creek syncline: RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Myers, C. W., 1981, Bedrock structure of the Cold Creek syncline area, in Myers, C. W., and Price, S. M., editors, Subsurface geology of the Cold Creek syncline: RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Myers, C. W., Price, S. M., Caggiano, J. A., Cochran, M. P., Czimer, W. J., Davidson, N. J., Edwards, R. C., Fecht, K. R., Holmes, G. E., Jones, M. G., Kunk, J. R., Landon, R. D., Ledgerwood, R. K., Lillie, J. T., Long, P. E., Mitchell, T. H., Price, E. H., Reidel, S. P., and Tallman, A. M., 1979, Geologic studies of the Columbia Plateau, a status report: RHO-BWI-ST-4, Rockwell Hanford Operations, Richland, Washington.

Neuman, S. P. and Witherspoon, P. A., 1972, Field determination of the hydraulic properties of leaky multiple aquifer systems: Water Resources Research, vol. 8, no. 5, p. 1284-1298.

Newcomb, R. C., 1961, Storage of groundwater behind subsurface Dams in the Columbia River basalt in Washington, Oregon, and Idaho: U.S. Geologic Survey Prof. paper 383-A, p. 15.

Newcomb, R. C., 1958, Ringold formation of Pleistocene age in type locality, the White Bluffs, Washington: American Journal of Science, v. 256, p. 328-340.

Packer, D. R., and Johnston, J. M., 1979, A preliminary investigation of the magnetostratigraphy of the Ringold Formation: RHO-BWI-C-42, Rockwell Hanford Operations, Richland, Washington.

Packer, D. R., and Petty, M. H., 1979, Magnetostratigraphy of the Grande Ronde Basalt, Pasco Basin, Washington: RHO-BWI-C-46, Rockwell Hanford Operations.

Price, E. H., 1981, Distribution of strain features within selected Yakima fold structures and extrapolation of their nature into the Cold Creek syncline area, in Myers, C. W., and Price, S. M., editors, Subsurface geology of the Cold Creek syncline: RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Reidel, S. P., 1978, The stratigraphy and petrogenesis of the Grande Ronde Basalt in the Lower Salmon and adjacent Snake River Canyon: Ph.D. dissertation, Washington State University, Pullman, Washington, 415 p.

Reidel, S. P., and Long, P. E., 1980, Discriminant analysis as a method of flow identification and correlation in layered basalt provinces: RHO-BWI-SA-69, Rockwell Hanford Operations, Richland, Washington.

Reidel, S. P., Ledgerwood, R. K., Myers, C. W., Jones, M. G., and Landon, R. D., 1980, Rate of deformation in the Pasco Basin during the Miocene as determined by distribution of Columbia River basalt flows: RHO-BWI-SA-29, Rockwell Hanford Operations, Richland, Washington.

Reidel, S. P., and Fecht, K. R., 1981, Wanapum and Saddle Mountains basalts of the Cold Creek syncline area, in Myers, C. W., and Price, S. M., editors, Subsurface geology of the Cold Creek syncline: RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Rietman, J. D., 1966, Remanent magnetization of the late Yakima Basalt, Washington State: Ph.D. dissertation, Stanford University, Stanford, California.

Siems, B. A., Bush, J. H., and Crosby, J. W. III, 1974, TiO₂ and geophysical logging criteria for Yakima basalt correlation, Columbia Plateau: Geol. Soc. Amer. Bull., v. 85, p. 1061-1068.

Strait, S. R., and Moore, B. A., 1982, Aquifer intercommunication in the Gable Mountain pond area, Hanford site, south-central Washington: RHO-ST-38, Rockwell Hanford Operations, Richland, Washington.

Swanson, D. A., and Wright, T. L., 1976, Guide to field trip between Pasco and Pullman, Washington, emphasizing stratigraphy and vent areas and intra-canyon flows of Yakima Basalt: in Proceedings, Geological Society of America, Cordilleran Section Meeting, Pullman, Washington, Field Guide 1., 33 p.

Swanson, D. A., Wright, T. L., Hooper, P. R., and Bentley, R. D., 1979a, Revisions in stratigraphic nomenclature of the Columbia River Basalt Group: U. S. Geological Survey Bulletin 1457-G.

Swanson, D. A., Wright, T. L., and Zietz, I., 1979b, Geologic aeromagnetic map and geologic interpretation of the west-central Columbia Plateau, Washington and adjacent Oregon: U. S. Geological Survey Geophysical Investigations Map GP-917.

Tallman, A. M., Fecht, K. R., Marratt, M. C., and Last, G. V., 1979, Geology of the separation areas, Hanford Site, south-central Washington: RHO-ST-23, Rockwell Hanford Operations, Richland, Washington.

Tallman, A. M., Lille, J. T., and Fecht, K. R., 1981, Suprabasalt sediments of the Cold Creek syncline area, in Myers, C. W., and Price, S. M., editors, Subsurface geology of the Cold Creek syncline: RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Waters, A. C., 1961, Stratigraphic and Lithologic variations in the Columbia River basalt: American Journal of Science, v. 259, p. 581-611.

Watkins, N. D., 1965, Paleomagnetism of the Columbia Plateaus: Jour. Geophys. Research, v. 70, p. 1379-1406.

Wright, T. L., Grolier, M. J., and Swanson, D. A., 1973, Chemical variation related to the stratigraphy of the Columbia River Basalt: Geol. Soc. Amer. Bull., v. 84, p. 371-386.

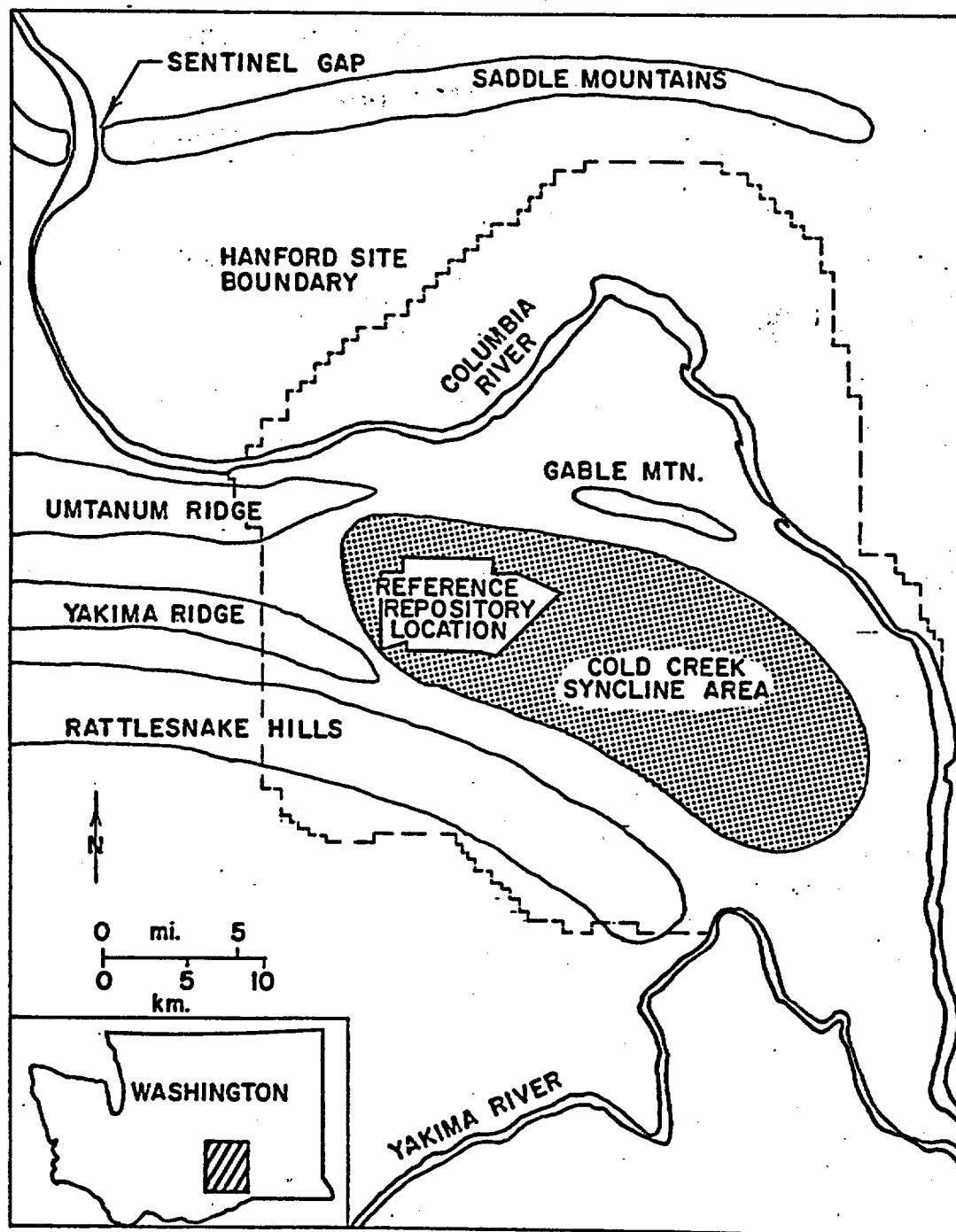


Figure 1. Location map of major geographical features and study areas, Pasco Basin, Washington.

Figure 2. General stratigraphy and stratigraphic nomenclature for the Pasco Basin, Washington (after Myers and others, 1979).

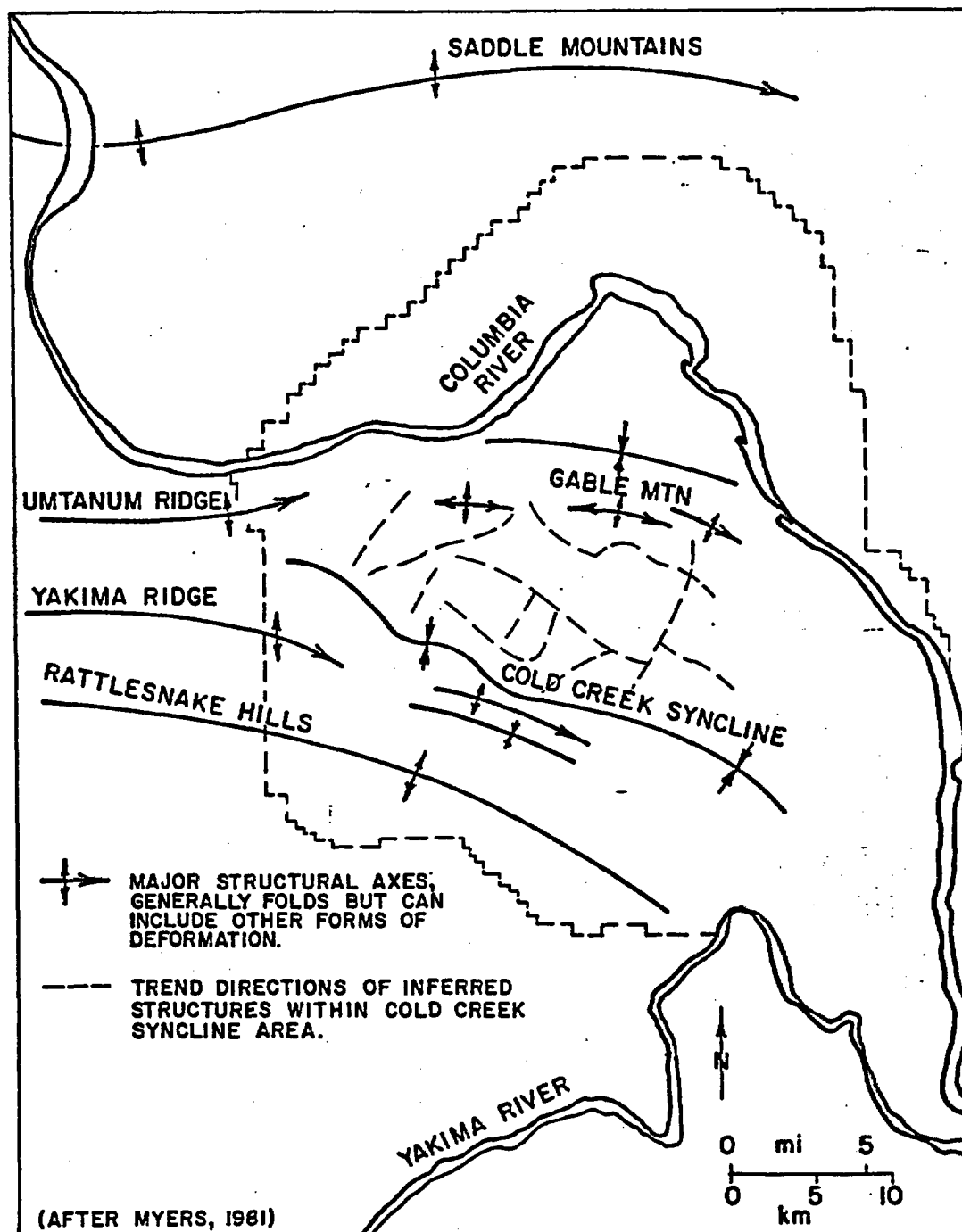


Figure 3. Location of major surface and possible subsurface structure, Cold Creek syncline and Pasco Basin, Washington.

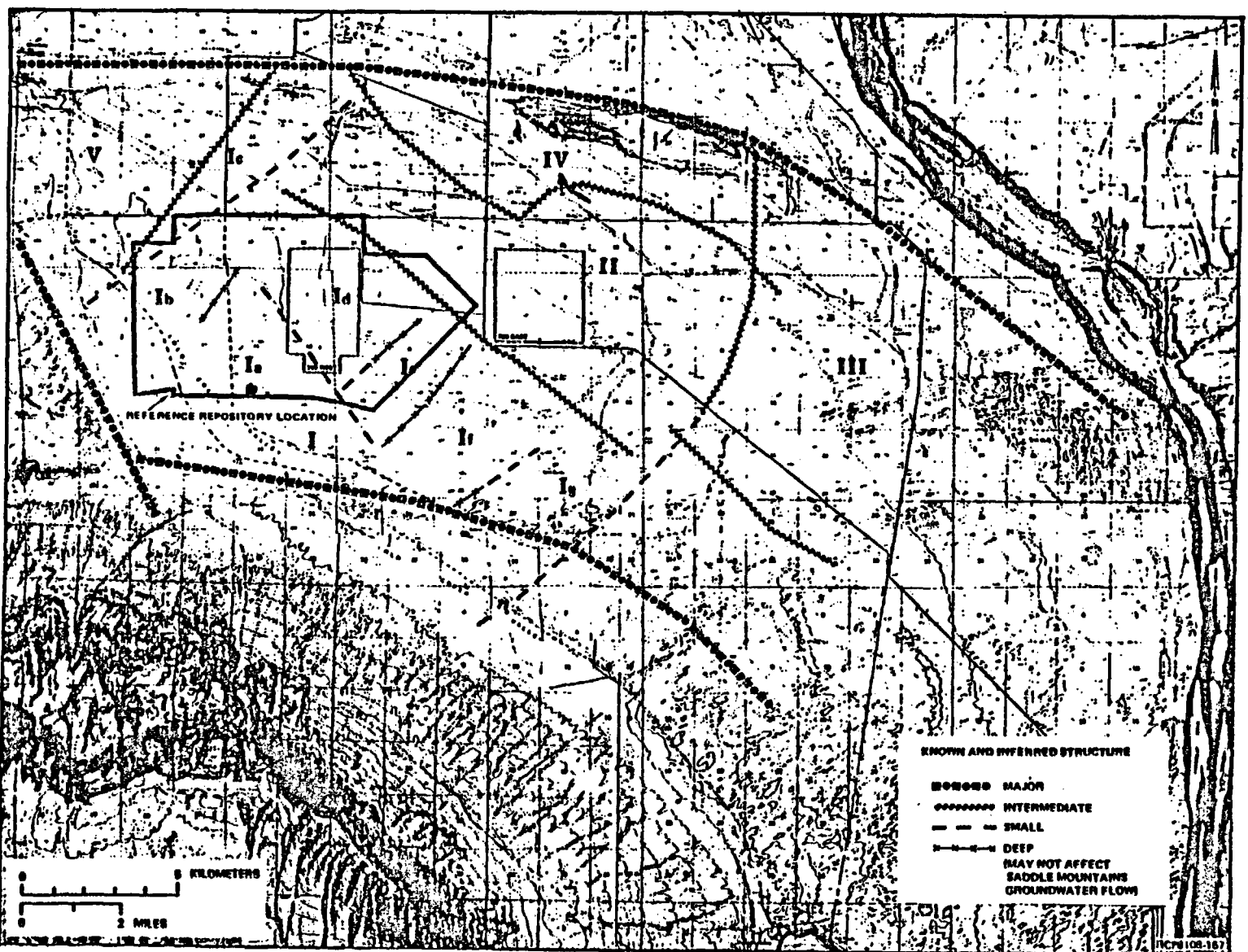


Figure 4. Location of known and inferred structures, Cold Creek Syncline, Pasco Basin, Washington

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APPENDIX M
SEISMIC HAZARD AT HANFORD

In determining the earthquake risk of a critical facility three elements are required. First is an estimate of the seismic hazard. In studying seismic hazards, we are concerned about the probability that an earthquake or its associated ground motion will occur at a site during a specified period of time. The exceedance probability is the probability that over some period of time an earthquake will generate a level of ground shaking greater than some specified level. The return period is the reciprocal of the annual probability of exceedance. These estimates are not meant to be used in a time predictive manner but rather represent average estimates for very long periods of time. The other two elements are (1) the seismic resistance and (2) the consequences of failure which may occur at the facility. This report discusses the first of these three topics, the seismic hazard. Initial discussion will be centered on seismic hazard in general. In addition there will be a brief review of three seismic hazard studies that have been completed for the Hanford region.

In general, seismic hazard is typically quantified as the probability (which may or may not have a distribution) that certain size earthquakes (either intensity or magnitude) or certain values of ground motion (such as peak acceleration) will occur during given intervals of time. Steps which are necessary to estimate the seismic hazard are: (1) the identification of seismic source zones (could be a specific fault); (2) the quantification of an earthquake occurrence model for each seismic source zone; (3) the quantification of a ground motion relationship and (4) a way of integrating numbers 1-3 to evaluate the seismic hazard at a site. Examples of programs by which seismic hazard can be estimated are those of Cornell and Merz (1974) and McGuire (1976).

An important part of completing a seismic hazard analysis involves the selection of an approach to incorporate the uncertainty of all input parameters into the analysis. In the definition of seismic source zones this includes all source zone alternatives with a certain likelihood of being correct (degree of belief), and the shape of each source zone alternative. For example, the existence of a specific seismic source zone may be relatively certain but the exact shape of the boundaries may be uncertain.

For the earthquake occurrence model the location and size of earthquakes for each source zone must be quantified. This includes an evaluation of the completeness of the seismic record for each zone. As an example, in one seismic source zone a magnitude 4.0 event may have been detectable for the past 50 years, while in another zone it may be a magnitude 5.0 event in 50 years because of a lack of seismic instrumentation in this region. In addition the earthquake recurrence must be defined for each zone. This includes the mean number of earthquakes and the size distribution. Uncertainty of the number of earthquakes must be assessed along with the ratio of large to small earthquakes (commonly called the "b" value). For very long periods of time an important factor may involve the likelihood that seismicity will increase or decrease with time.

In dealing with the ground motion attenuation relationship, the investigator is usually faced with the problem that little if any strong ground motion data is available in the region of study. A mean ground motion relationship should

be defined along with the uncertainty in this mean value. When little or no data exists, other studies on attenuation can be used to help assess how strong ground motion will attenuate.

Two types of uncertainties exist in the parameters discussed above. These are random and systematic uncertainty. Random uncertainty involves the independent variability (inherent in nature) of a parameter from earthquake to earthquake. An example is the peak acceleration variability given the same size earthquake at the same distance. Systematic uncertainty involves the possible mistakes in the assumptions of the hazard model. An example would be an incorrect mean attenuation model or an incorrect seismic source zone. In completing a seismic hazard analysis, it is common to keep these two types of uncertainties separate, so a judgement can be made on the best estimate (with random variability included) and the distribution about this best estimate due to possible systematic errors.

Through many different sensitivity runs, major assumptions and parameter choices that lead to significant variations in the predicted hazard at the site in question can be identified. Discussed below are some sensitivity results of the Systematic Evaluation Program (NUREG/CR-1582) and from studies by Perkins (1981).

As part of the Systematic Evaluation Program (SEP) a comprehensive study was undertaken by Lawrence Livermore National Laboratory and the Tera Corporation to define the response spectrum of different return periods at a number of power plant sites. This study included the use of expert opinion (10 experts) in defining seismic source zones and the amount of activity in each zone. Results of sensitivity tests from this program are listed in numerical fashion below.

1. The nearest seismic source zones to a site are the most important. Variability in a particular source zone is particularly important if a site lies within a potential source zone.
2. In terms of seismicity - the level of seismicity was found to have relatively little impact on the results. However, the relative size distribution (the "b" value) was found to be important at long return periods. Including the uncertainty in "b" values increases acceleration 30 to 50% at return periods of 4000 years.
3. In terms of the upper magnitude cutoff, this, like the "b" values becomes important at long return periods. A combination of a low "b" value and high upper magnitude cutoff (causing shorter return periods for larger magnitude earthquakes) was found to be very important at long return periods.
4. The ground motion attenuation model was found to be extremely important, particularly in how one accounts for the amount of uncertainty.

General conclusions from the SEP are that variations are greatest for longer return periods; periods in excess of about 10,000 years. If extrapolation beyond the existing data is required then significant differences could result from small variations in input parameters.

Perkins (1981) has also studied the effect of changing return periods from single parameter variations. He found that including the uncertainty in the ground motion model increases the peak acceleration by a factor of 2 at return periods of thousands of years or more. To get this level of increase in peak acceleration from other parameters requires very drastic parameter variations. For example, to double the peak acceleration one would need a 10 fold increase in level of seismicity or a change in the maximum magnitude from 5.0 to 8.5. Perkins (1981) concluded that at long return periods, uncertainty in ground motion swamps reasonable changes in seismicity parameters.

How do these comments impact the High Level Waste Repository (HLWR)? The answer to this question will depend on how long a return period one requires for various aspects of the HLWR. If the surface facility needs to be operational for about 100 years and the reliable confidence in return period is out to about 10,000 years, then a judgement on what peak acceleration has about a 1% chance of occurring in 100 years can probably be made. However if return periods in excess of about 10,000 years are required then the specification of design values will require considerable judgement regarding the input parameters, or as an alternative the design levels selected may be very conservative.

Discussed below are three seismic hazard studies which have some information on seismicity parameters of the Hanford region.

1. Woodward-Clyde, 1980, "Factors Influencing Seismic Exposure of the Southeast Washington Region": In this study earthquakes are assumed to occur only in source areas, not on specific faults or structures. The Hanford area is in a diffuse source region except for specific source zones near Walla Walla and Ellensburg. Shortcomings of this study are that no uncertainty is included in the definitions of source zones or in the levels of seismicity. The peak acceleration values may not include uncertainty, although tests were made to show what effects including this uncertainty would have (if they were not included). Results of this study conclude that a mean peak acceleration of 0.16g has a return period of about 1200 years. For a 10,000 year return period this would imply a mean acceleration of near 0.25g.
2. USGS Open File Report 8-471, 1980, "Probabilistic Estimates of Maximum Seismic Horizontal Ground Motion on Rock in the Pacific Northwest and the Adjacent Outer Continental Shelf": This report uses both geologic and seismologic data to define seismic (seismogenic) source zones. Peak acceleration values are not generated for the Hanford region, although levels of seismicity are defined. The shortcomings of this report include lack of sensitivity regarding the various source zones and seismicity levels assumed. From the earthquake occurrence rates assumed one finds that a magnitude 6.1 earthquake has a return period of about 14,000 years within 25 km of the HLWR. Where peak acceleration values are determined, these investigators do not account for possible systematic attenuation difference between the Pacific Northwest and California, and do not include ground motion uncertainty.
3. Woodward-Clyde, 1981, "Seismic Exposure Analysis for the WNP-2 and WNP-1/4 site, Amendment 18 to the WNP-2 Final Safety Analysis Report": In contrast to the 1980 Woodward-Clyde report, earthquakes in this analysis are

modeled as occurring on known geologic structures (faults). No earthquakes are assumed to have the potential for occurring randomly (in a source zone) and only faults within 50 kilometers of the site are thought to contribute to the hazard. This approach allows for the incorporation of some uncertainties and alternative hypotheses, including the tectonic model, fault geometry, potential source segmentation, source capability, and maximum magnitude on each fault. In addition, uncertainty is included in the ground motion attenuation relationship. Shortcomings of this report include the lack of sensitivity on the exclusion of alternative seismic source zones, the lack of variability on earthquake recurrence on individual structures, the potential that the level of earthquakes below a magnitude 6.0 are underpredicted, and the possibility that the mean attenuation rate is incorrect for the Columbia Plateau. The conclusion of this report is that for the WNP-2 site, that a peak acceleration of 0.25g has a return period of about 9,000 years (3700 years at 90 percent confidence level). It is difficult to transfer this value to other areas in the Hanford region because the peak acceleration value is sensitive to the distance of particular geologic structures. For example, the Gable Mountain structure contributes about 75% with the Rattlesnake structure contributing about 16% for the WNP-2 site. For the HLWR these numbers might change due to Gable being further away and Rattlesnake being closer.

The NRC staff concluded (WNP-2 SSER) that sensitivity tests would have to be completed before more confidence in the estimates of the ground motion hazard could be made regarding the 1981 Woodward-Clyde report. This is essentially true for all three seismic hazard studies. It will be important to set a target if a seismic hazard analysis is going to be used to help reflect a design level for the HLWR. This means that it will be very difficult to have high confidence in a particular return period from a seismic hazard analysis unless sensitivity tests are completed showing which parameters have the largest impact on the hazard. For the 1981 Woodward-Clyde report the return period for the WNP-2 site is on the order of 1,000 to 10,000 years (a specific number such as 9000 would be difficult to support). For longer return periods the spread in confidence on these return periods becomes even larger due to uncertainty in the analysis.

In conclusion, seismic hazard analysis study is a powerful tool, particularly in a region where there are no obvious seismic source zones, in assessing relative levels of ground motion in a given region. It can be very useful in helping assess a specific level of design for a site particularly if wide ranging sensitivity tests are completed.

REFERENCES

- Cornell, C.A., and H. Merz, 1974, Seismic Risk Analysis of Boston, Jour. Struc. Div., Proc. Am. Soc. Civil Engineers, V107, p. 2027.
- McGuire, R.L., 1976, FORTRAN Computer Program for Seismic Risk Analysis U. S. Geological Survey Open-File Report 76-67.
- Perkins, D.M., 1981, Effect of Changing Return Periods on Probabilistic Ground Motion, Proc. Workshop on Seismic Performance of Underground Facilities, E.I. du Pont de Nemours & Co., p. 183.
- United States Geological Survey, 1980, Probabilistic Estimates of Maximum Seismic Horizontal Ground Motion on Rock in the Pacific Northwest and the Adjacent Outer Continental Shelf, Open-File Report 80-471.
- United States Nuclear Regulatory Commission, 1980, Seismic Hazard Analysis, NUREG/CR-1582 Vols. 2, 3, 4, 5.
- United States Nuclear Regulatory Comm., 1982, Safety Evaluation Report related to the operation of WPPSS Nuclear Project No. 2, NUREG-0892, Supp. No. 1.
- Woodward-Clyde Consultants, 1980, Factors Influencing Seismic Exposure of the Southeast Washington Region, prepared for WPPSS.
- Woodward-Clyde Consultants, 1981, Seismic Exposure Analysis for the WNP-2 and WNP-1/4 site, Appendix 2.5K, Amendment 18, WNP-2 FSAR.

APPENDIX N
EARTHQUAKE SWARMS IN THE COLUMBIA PLATEAU

One seismicity pattern that has evolved since 1969 (the start of microearthquake monitoring) involves the occurrence of earthquake swarms within the Columbia Plateau. An earthquake swarm is defined as a sequence of earthquakes in which the size and number of events gradually increases, then decreases, with time, with no outstanding main shock (Mogi 1963). Of particular importance is the cause of these microearthquake swarms, and how they may or may not impact the siting of the high level waste repository (HLWR).

Past swarm activity in the Columbia Plateau has been discussed by Pitt (1971), Malone et. al. (1975), Rothe (1978), and as part of Appendix 2.5J of Amendment 18 to the Washington Nuclear Project No. 2 (WNP-2) Final Safety Analysis Report. This discussion will concentrate on the swarm earthquake activity within the Pasco Basin. It is also assumed for this discussion that the HLWR will be located just west of the 200W liquid waste disposal operation within the Cold Creek Syncline area of the Pasco Basin. The Pasco Basin is delineated by the dotted line of Figure 1.

Within the Plateau, swarm earthquakes are defined by a clustering of events in both space and time. Swarms are typically localized to an area of a few kilometers, within the upper three kilometers of the crust. Figure 2 displays a plot of swarm earthquakes as defined by Woodward-Clyde Consultants for the WNP-2 site. Within the Pasco Basin swarm events have occurred south-southeast of Saddle Mountains, along the Columbia River (Wooded Island and North of Gable Mtn and Gable Butte), and most importantly near the 200W disposal area within 10 kilometers of the HLWR. Within these areas the largest earthquake was the October 25, 1971 $M_c=3.8$ event at Coyote Rapids. M_c is a duration magnitude (based upon earthquake coda length) that was developed by the University of Washington. The largest earthquake near the 200W disposal area was the $M_c=2.44$ event on September 8, 1979, while the largest swarm earthquake recorded in the Columbia Plateau was the December 20, 1973 $M_c=4.38$ Royal Slope event.

Both Malone et al (1975) and Rothe (1978) have concluded, based upon focal mechanism solutions of individual swarm sequences, that slip takes place on a number of different fault planes. Fault plane solutions also indicate that

slip is in response to a roughly uniform north-south compressive stress field. There have been different ideas concerning the type of fractures this slip is occurring on. Rothe (1978) suggests that slip takes place on columnar joints, while Woodward-Clyde (1982a) favors slip along tectonic fractures within the basalt. In either situation, any judgment concerning the size of future swarm seismicity must take into account the uncertainty in the dimensions of potential fracture surfaces that will be involved in any one swarm event.

As shown in Figure 2, it appears that the swarms within the Columbia Plateau are not occurring randomly. However, no mechanism has been found which can explain the cause of all the swarms. The Pasco Basin has relatively few occurrences of swarms compared to the area to the north near the Saddle Mountains and Frenchman Hills. One assumption is that swarms occur only on large anticlines. However, swarms have not occurred on the topographic expressions of all the largest known anticlines. In addition some

investigators have concluded that they find no well defined planar trends that might define active faults (Woodward-Clyde 1982a). Various investigators (Turcotte, 1975; Rothe, 1978; Woodward-Clyde, 1982a) have suggested that ground water level changes may be a triggering mechanism for the swarm seismicity. As shown in figure 3, a visual inspection reveals that the majority of swarm events have occurred in areas of irrigation or in areas bordering (within 5 kilometers) irrigation. However, this does not explain all the swarms because some swarms have occurred in non-irrigated areas.

In general, the following items may facilitate the occurrence of swarms in the Pasco Basin. The region must be fractured, the region is likely to have some history of seismicity (many swarms have occurred repeatedly at the same place; Wooded Island is one example), and the stress level must be relatively close to the strength of the stressed material. With this in mind, the swarms (as discussed below) may impact the HLWR in both the short term (construction operation) and long term (life of repository).

The observation that swarms have occurred within 10 kilometers of the HLWR leads one to the conclusion that fractures exist within this region, and that some fractures are close to (or have exceeded) their failure strength. In the short term, the mining operation may cause enough stress perturbations that intersected fractures may move. This could result in degradation of the mine openings or damage to mining equipment. In the long term repeated movement along fractures could lead to modification of the route or rate of groundwater movement. It could be argued that an individual swarm event or sequence produces only minor (fractions of centimeters) amounts of displacement. However, because of the long life of the repository (1,000 to 10,000 years) it is possible that many repeated swarms may affect the HLWR. Critical information will be obtained during the exploratory drilling, determining the extent of fractures at the HLWR.

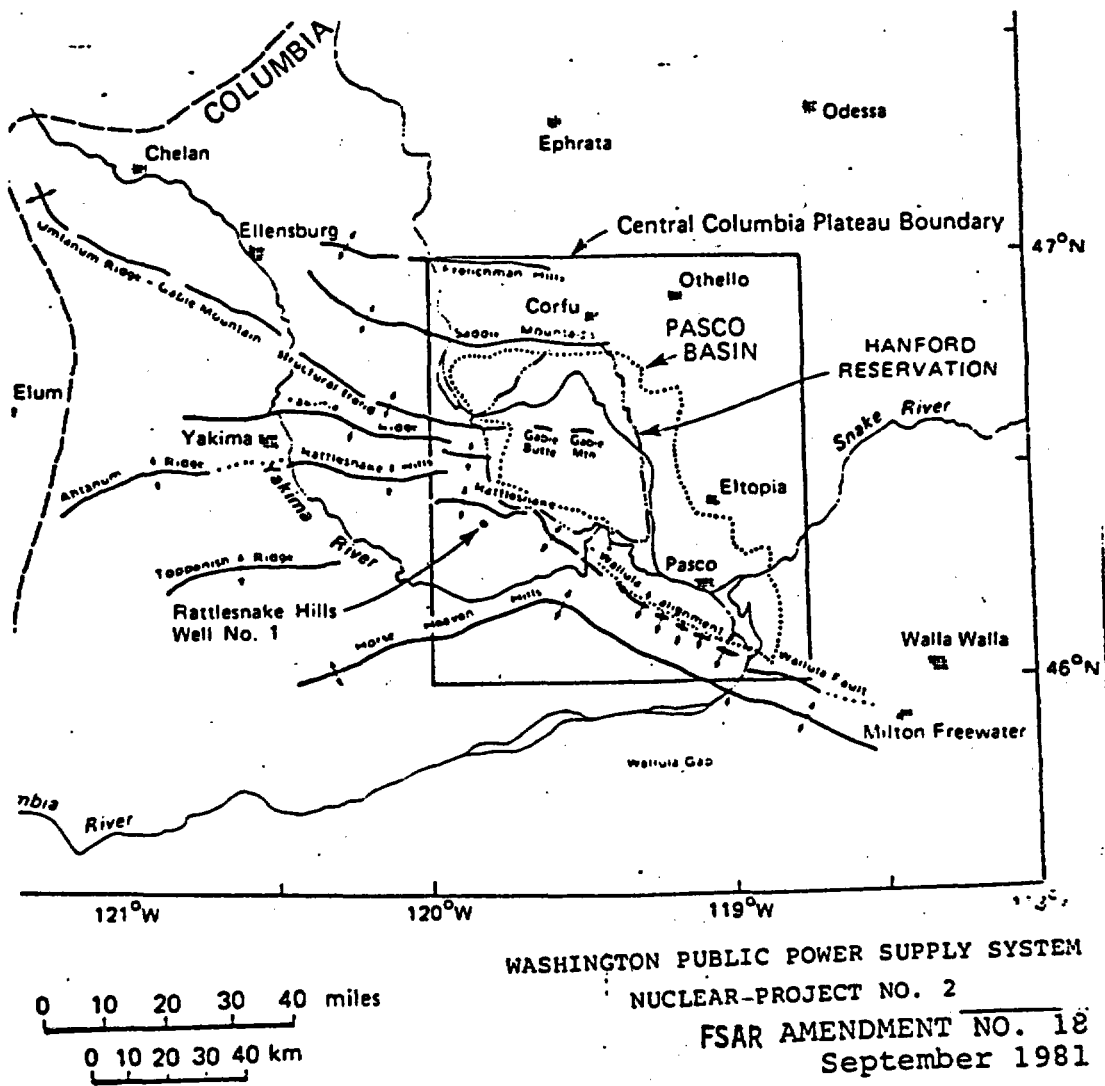
The nature of the ground motion resulting from the occurrence of a swarm earthquake is difficult to assess. Ground motion is likely to be of short duration and high frequency although the peak acceleration may be relatively high. For example, Woodward-Clyde (1982b) has estimated 0.31g (84th percentile) for a $M_L = 4.0$ event at a hypocentral distance of 3 kilometers. A study by McGarr et al. (1981) has also documented short duration, high frequency, high peak acceleration (up to 11.7g) strong ground motion in the near field of small magnitude earthquakes. McGarr et al. (1981) also observed that none of the studied events significantly damaged the mining excavations where the ground motion was observed. He suggested that it may be more reasonable to assess the damage potential of swarm earthquakes in terms of peak velocity. A general comment might be that if a particular system or component either on the surface or in the subsurface, is sensitive to short duration, high frequency ground motion, then more detailed investigations (to define more accurately the ground motion conditions) may be prudent.

In conclusion, swarm earthquakes have occurred within 10 kilometers of the HLWR. These swarms could impact the construction of the repository in the short term, and could increase the route and rate of groundwater movement through the repository in the long term.

REFERENCES

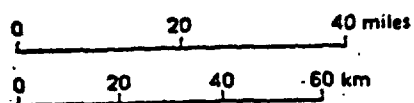
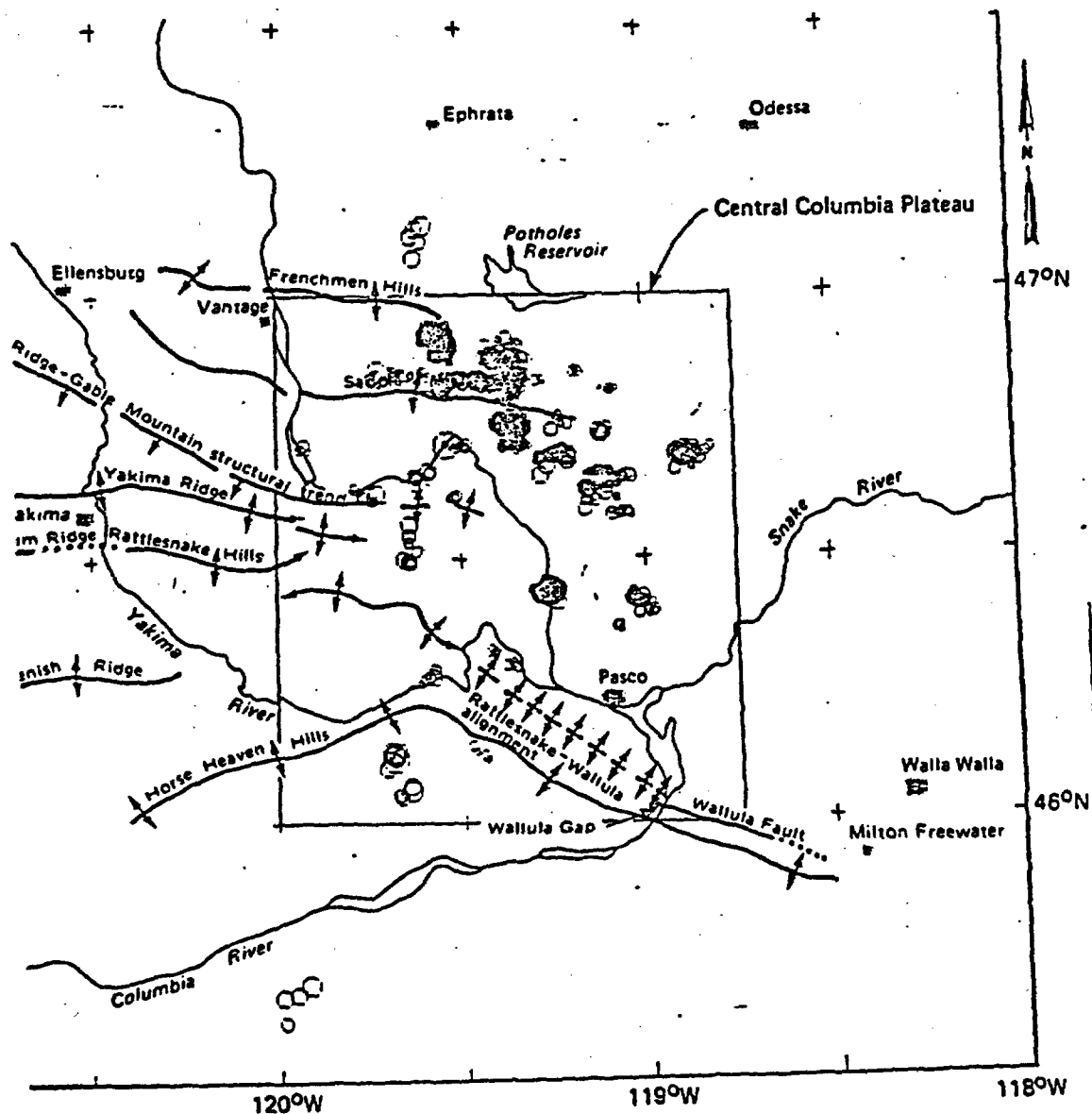
- Malone, S.D., Rothe, G.H., and Smith, S.W., 1975, Details of microearthquake swarms in the Columbia Basin, Washington: Bulletin of the Seismological Society of America, v. 65, p. 855-864.
- McGarr, A.R., Green, W.E., and Spottiswoode, S.W., 1981, Strong Ground Motion of Mine Tremors: Some Implications for Near-Source Ground Motion Parameters, Seismol. Soc. Amer. Bull., V 71, p. 295.
- Mogi, K., 1963, Some discussions on aftershocks, foreshocks and earthquake swarms - the fracture of a semi-infinite body caused by an inner stress origin and its relation to the earthquake phenomena (third paper): Earthquake Research Institute Bulletin, v. 41, p. 615-658.
- Pitt, A.M., 1971, Microearthquake activity in the vicinity of Wooded Island, Hanford region, Washington: U. S. Geological Survey, Preliminary Open-File Report prepared on behalf of the Richland Operations Office, U. S. Atomic Energy Commission, 23 p.
- Rothe, G.H., 1978, Earthquake Swarms in the Columbia River Basalts: Ph.D. dissertation, University of Washington, Seattle, 181 p.
- Turcotte, F.T., 1975, Microearthquake statistical correlation study Hanford Reservation, Washington: Report prepared for the Washington Public Power Supply System by Weston Geophysical Research, Inc., Westboro, MA, 14 p.
- Woodward-Clyde Consultants, 1982a, Analysis of the Instrumental Seismicity of the Columbia Plateau, Report prepared for Washington Public Power Supply System.
- Woodward-Clyde Consultants, 1982b, Response to NRC Question Q361.16 WNP-2, Report prepared for Washington Public Power Supply System.

Figure 1



Extent of the Pasco Basin defined by the dotted line

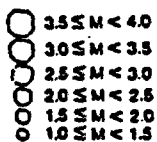
Figure 2



WASHINGTON PUBLIC POWER SUPPLY SYSTEM
NUCLEAR PROJECT NO. 2

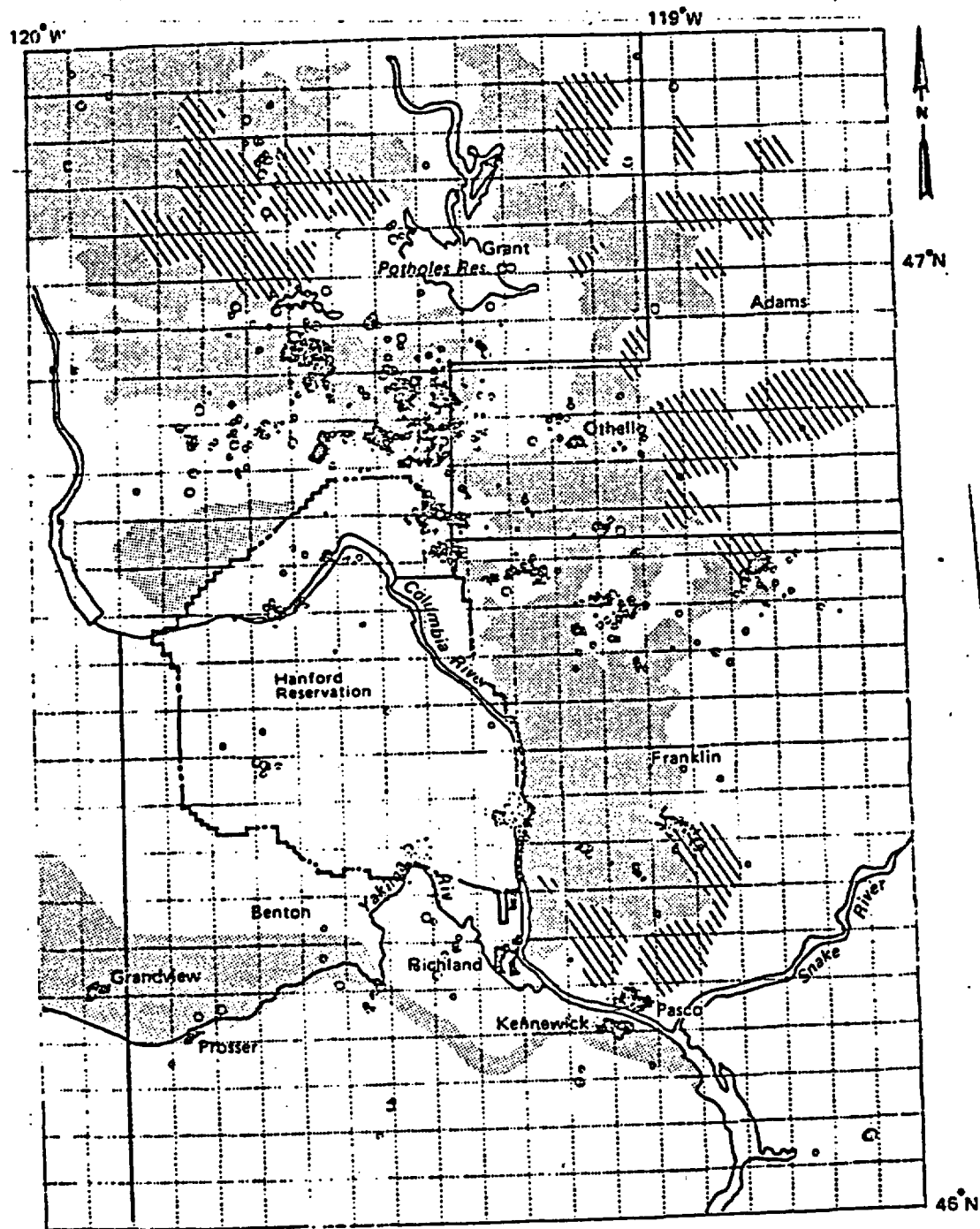
FSAR AMENDMENT NO. 18
September 1981

LEGEND



Swarm earthquakes in the Pasco Basin region

Figure 3



0 10 20 30 40 50 km

EXPLANATION

- Areas with potential for irrigation
- Areas irrigated with canal water
- Areas irrigated with ground water

WASHINGTON PUBLIC POWER SUPPLY SYSTEM
NUCLEAR PROJECT NO. 2

FSAR AMENDMENT NO. 18
September 1981

Swarm seismicity and areas of irrigation

N-7

APPENDIX O
SEISMIC GROUND MOTION AT DEPTH

In siting the High Level Waste Repository (HLWR) it will be necessary to assess both the potential for free field ground motion and ground motion at depth (where a large portion of the facilities will be). This topic report will attempt to assess available information on observations of ground motion at depth. A large portion of this information is contained within the proceedings to the Workshop on Seismic Performance of Underground Facilities (1981) although attempts have been made to obtain empirical observations of ground motion at depth (such as Vortman and Long, 1982).

In general, as discussed by Pratt (1981), McClure (1981), and Dowding and Rozen (1978), there have been numerous observations that underground structures suffer less damage than surface structures during strong motion shaking. A large portion of this information, however, is qualitative rather than quantitative. In general damage to subsurface facilities can be caused by one or more of the following: (1) damage by ground failure (landslide, liquefaction), (2) damage from fault displacements and (3) damage from strong ground motion (Dowding and Rozen, 1978). Since the surface portion of the HLWR will be at a depth of about 1 kilometer ground failure can be essentially eliminated.

Dowding and Rozen (1978) have estimated the peak acceleration and velocity in tunnels that have experienced seismic shaking. Their conclusion is dependent upon McGuire's (1974) attenuation relationship. They conclude that at peak surface accelerations which are expected to cause damage to surface facilities (up to 0.40g), there is little damage to tunnels. They also state that "shaking damage can be eliminated by stabilizing the soil or rock around the tunnel . . . especially by improving the contact between the lining and the rock" (Dowding and Rozen, 1978).

Stevens (1977) has studied the effects of earthquakes on underground mines. He states that severe damage is inevitable when a mine or a tunnel intersects a fault along which movement occurs during an earthquake. Damage due to shaking may occur in the epicentral area and is least likely to occur in fresh competent bedrock.

Various authors have documented (WCC, Iwasaki et al. 1977) that ground motion decreases with depth. However, the majority of these recordings have been in soil, whereas the HLWR will be in bedrock. Iwasaki et al. (1977) recorded 10 earthquakes at 3 depth levels (0M, 80M, 120M) in sandstone and siltstone. In general the ground motion at the depths of 80 and 120 m are less than at the surface. In reviewing this sparse data, there is some slight indication that the depth reduction factor may be magnitude and distance dependence (more reduction for shorter distances or smaller magnitudes). The closest distance of this data set is 40 kilometers.

A large amount of information on downhole ground motion has recently become available from Underground nuclear tests (Vortman and Long, 1982). Approximately 3,000 records are available, comparing measurements at the surface to those at depths ranging from 61 meters to 762 meters.

Comparisons (between surface and subsurface) have been made using vector peak accelerations, velocity, and displacement; vector response spectrum, and multiple peaks of vector acceleration, velocity and displacement. Recordings

have been acquired in a variety of mediums such as alluvium, shale, limestone, tuff and granite.

Comparisons in Vortman and Long (1982) are tabulated for nuclear shots at Pahute Mesa and are shown in the report figures for both Pahute Mesa and Yuca Flats. For vector peak acceleration, velocity and displacement there is a trend of decreasing motion with depth (for all site conditions), averaging to be factors of 1.92, 1.73, 1.54 for vector peak acceleration, velocity and displacement at a depth of 300 meters. Similar reductions factors are found for multiple vector peaks (such as the average of the highest 15 peaks) of acceleration, velocity and displacement.

Ratios of vector response spectrum are also shown in Vortman and Long (1982). These response spectra demonstrate that at a particular site, there are one or two frequency bands that have very large reductions in the downhole ground motion.

The data set of Vortman and Long (1982) is by far the most extensive set of quantitative information on downhole strong motion recordings. The BWIP applicant should closely follow the continued processing of this information and assess what data can be used to estimate the reduction factors for the HLWR at Hanford. One area for further work will involve the impact, that these recordings are from explosions instead of earthquakes. Are the results transferable from one to the other?

The impact of potential fault displacement at depth can be initially assessed when test drilling is completed. Until that time only qualitative statements can be made, such as the synclines around Hanford tend to have less faults compared to the anticlines.

In addition, it would be prudent for the BWIP applicant to attempt downhole recordings (if possible) at the HLWR site. This would be the best quantitative information on how ground motion (and at what frequencies) decreases with depth.

In conclusion, the qualitative information contained in the Workshop on Seismic Performance of Underground Facilities (1981) along with the quantitative data of Vortman and Long (1982) indicate that ground effects and amplitude decrease with depth. Exact quantification of these factors for the HLWR at Hanford can be best assessed by recordings at the BWIP site.

REFERENCES

1. Dowding, C.H. and A. Rozen, 1978, "Damage to Rock Tunnels from Earthquake Shaking," J. Geotechnical Eng. Div., Am. Assoc. Civil Eng., vol. 104, no. GT2, p. 175-191.
2. Iwasaki, T., S. Wakabayashi, and F. Tatsuoka, 1977, "Characteristics of Underground Seismic Motions at Four Sites around Tokyo Bay." Wind and Seismic Effects, Proceedings of the Eighth Joint Panel Conference of the U. S. Japan Cooperative Program in Natural Resources, NBS Special Bulletin 477, pp. III-41-III-56.
3. McClure, C.R., 1981, Damage to Underground Structures During Earthquakes, Proceedings Seismic Performance of Underground Facilities, E.I. du Pont de Nemours & Co., p. 75, R. K., 1974.
4. McGuire, Seismic Structural Response Risk Analysis, Incorporating Peak Response Regression on Earthquake Magnitude and Distance. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA.
5. Pratt, H.R., 1981, Earthquake Damage to Underground Facilities and Earthquake Related Displacement Fields, Proceedings Seismic Performance of Underground Facilities, E.I. du Pont de Nemours & Co., p. 43.
6. Stevens, P.R. (1977), "A Review of the Effects of Earthquakes on Underground Mines." U. S. Geol. Survy. Open-File Rept. 77-313, 47 pp.
7. Vortman, L.J., and J. W. Long, 1982, Effects of Repository Depth on Ground Motion - The Pahute Mesa Data, Sandia National Laboratories, SAN082, 0174.
8. Woodward-Clyde Consultants, 1981, Effective Peak Acceleration for Nuclear Power Plant Design; Technical proposal on Engineering Characteristics of Ground Motion, submitted to the U. S. Nuclear-Regulatory Commission.

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. 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. The objectives of this review are:

- (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 in the literature 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 of canister lifetime and thus indicate how 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 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 (Fe_3O_4) or hematite (Fe_2O_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 values. 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°C while repository conditions are calculated to range from 300°C to 65°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 so that a 25-30 mm thick overpack would protect the waste 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 corrosion rates are probably also higher unless the mechanisms are different. This study also suggests that air and steam would corrode a canister less than 1 cm during the canister's first 100 years in a repository.

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 5, a canister would need to be 1.8 to 3.3 cm thick 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 to 100 times. He found the variation in increase rates K to depend on three factors.

$$K = F(E_r, E_d, E_p)$$

E_d is the destructive effect of particulate radiation. It induces lattice defects in both metal and oxide. E_p 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 by two orders of magnitude when O_2 concentrations increase from 0 ppm to 1.5 ppm (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 (O_2^- , O_2^+ , O_4^- , O_4^+), ionic clusters ($\text{O}_2^- (\text{O}_2)_n$), and ozone (O_3). Oxides of nitrogen will also be formed: N_2O_5 , NO_3 , N_2O_3 , N_2O_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.

In sum, gamma radiation will result in several simultaneous changes in the iron system. 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 dissolved in basalt water are concentrated by evaporation (due to the heat from the waste products) prior to full resaturation, containers may well be subjected to conditions similar to those in brines.

Heat Transfer. Another important parameter affecting 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.

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

- (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, carbon steel is corroded under heat transfer conditions, although carbon steel may be passive isothermally. 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 4×10^4 and 4×10^5 kcal/m²-hr, respectively. The test solution has 0.1 m NaOH which yields 4000 ppm anions. This is nine times more concentrated than fresh basalt water and also contains dissolved O₂.) After 50 hours, pitting depth ranged an average 5 to 10 μm with a maximum pit depth of 40×10^{-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 $\mu\text{mho-cm}$ (Anderson). This places basalt in the 5 $\text{mg/dm}^2\text{-day}$ 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^2 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, thus 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 straightforward 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 the canister will be heated to 1000°C as the vitrified waste is poured into it, and will slowly cool to ambient temperatures. The nature of the oxide film formed is unknown. However, one can guess that it may be similar to a mill-scale 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 initially initiate localized attack, 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 and Ison found that pitting depth increased by a factor of 2 for a pickled surface over an untreated surface (Butler and Ison). A 4-month Belgian study of cast irons in a humid clay atmosphere showed a corrosion increase from 51 mg/dm^2 weight loss to 234 mg/dm^2 for grade 42 iron when mill-scale was removed. Similarly, grade 60 iron corrosion increased from 88 to 275 mg/dm^2 when mill-scale was removed (Dresselaers)*. All that can be concluded from these studies, then, is corrosion depends on the nature of the scale (Evans). Canister processing may

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

need to be tailored to produce a desirable scale. Corrosion tests should include the scales expected on production containers.

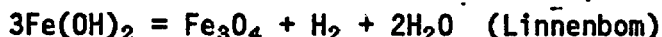
Assuming an optimal corrosion film, to determine long-term behavior in a repository, specific information is needed about scale adherence properties, integrity (ability to withstand stresses without cracking or undulating) and the chemistry of local repository water attacking cracks in the film.

Within the literature, there are discrepancies as to whether or not a high temperature and alkaline environment will produce an adherent scale. Huijbregts *et al.* have shown evidence that at 250°-300°C, solutions which are either deaerated (4 ppb O₂) or undeaerated and weakly alkaline (3×10^{-2} to 10^{-5} N NaOH), produced loose spalling oxide (Huijbregts). In a similar 3-month study, Potter and Mann saw some spalling on samples, but not all. The double-layered oxide formed in this experiment was 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 O₂. Steam and water formed oxides of different morphology, but both formed in accordance with parabolic rate laws (Effertz). Alloying elements also affect 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 10 (Bureau of Reclamation, 1965). 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). The corrosion of grey iron, however, may 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, Huijbregts *et al.* show about 50% nonadherent oxide. A probable mechanism to explain this loss involves the oxidation of iron to ferrous hydroxide (Fe(OH)₂). Ferrous hydroxide is usually ionized as Fe²⁺ and OH⁻ ions making it highly water soluble (see

Table 6). At ambient temperatures and anoxic conditions, ferrous hydroxide is the primary corrosion product (Bloom, Linnenbom). At high temperatures (60-250°C), ferrous hydroxide will rapidly oxidize to magnetite via the Schikkor 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 Schikkor 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_2 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_2 (Berge). An additional possibility in this situation is complete reduction of magnetite back to iron (Barkman). Magnetite reduction, however, 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 have 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 interstices 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 Fe(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 Cl^- and 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 (Townsend, 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 FeCl_2 from the crack, or (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 cannot 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 drastically reduced by vacuum arc remelting or electroslag remelting of the carbon steel/cast iron to remove impurities. Yet localized stresses and scratches cannot 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 $\mu\text{m}/\text{year}$ (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). Similar changes might be expected for the thick welds (up to 25 cm) considered in the past for BWIP.

Cramer and Carter also ran a 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 cannot readily be used to model behavior in basalt, particularly since it is not known to what extent dissolved gases (CO_2 , SO_2 , etc.) were responsible for corrosion rates.

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

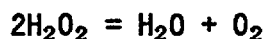
t = time in years

p = soil resistivity in ohm-cm

A = exposed surface area in ft^2

$a = 0.16$ for steel and 0.22 for cast iron

In a repository environment radiolysis can, at least in principle, reduce localized corrosion rates. Radiolysis in a crevice can consume H^+ at the same time it increases the pH in the crevice and the H_2O_2 reduces the differential by the reaction:



Both consumption of H^+ and production of O_2 in the occluded region tend to slow 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_2 will compete with the Cl^- 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_2O_2 (Townsend).

Radiolysis will also supply H_2 and H^+ within a pit (Glass). Hydrogen radical will readily combine, perhaps with the H^+ 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_2 (Pourbaix). The effect of H_2 from either or both of these sources will be to restrict the decrease in pH (by scavenging excess H^+). 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 still unknown.

The conclusions drawn from a literature assessment of localized corrosion indicate that analyses upon which licensing 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 verify failure modes and corrosion rates (Carter, 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 mechanisms 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).

Existing active paths in an alloy are formed by microsegregation and precipitation within a metal, usually at grain boundaries. Local galvanic cells weaken 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).

Active paths generated by strain 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 (decarburization 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 play 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 mega newtons/m² (100,000 psi), while steels less strong appear uniformly resistant. Cracking rate increases with temperature and Cl⁻ concentration, but the critical stress factor (K_{ISCC}) does not.

In sodium hydroxide solutions, cracking occurs 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/m² (Newby 1982). It will need to be determined, however, 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 cannot 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 and having different corrosion potentials, thus establishing an electrochemical cell. There should be little reason to worry about this, however, if waste canister, overpack, and metal rail upon which the canister is to be seated are all made 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, 50% of the corrosion to iron 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 pipes creating "tubercles." They also deposit 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 autotrophic 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 autotrophic 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 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, several conditions present in a repository will accelerate on corrosion rates. 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, to an unknown extent, the salts dissolved in repository waters. A best case would be to assume that this concentration will be negligible; a 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.

Occluded cell corrosion is expected to be the dominant mode of corrosive attack. 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 O₂ free basalt water data) to 11 (Romanoff, 1968, derived from soil corrosion data).

General corrosion, whether its rate follows a linear or parabolic 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 corrosion rate predicted for the canisters is satisfactory, an unacceptable number might fail to meet regulatory criteria 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 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 illustrates storage panels between drifts (BWIP Project View Graph 1982). Figures 8 and 9 give an example of a repository layout with dimensions.

Because of the requirements of 10 CFR Part 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

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

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 current BWIP findings:

- (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 Project 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 (BWIP Project View Graph 1982).

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 SCR refers to a simplified waste package 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, in spite 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 of 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 4 cm to 25 cm (BWIP View Graph 1982; Newby 1982; Newby 1981).

REFERENCES

1. Anderson, W. I., Corrosion Tests of Canister and Overpack Materials in Simulated Basalt Groundwater, Rockwell Hanford Operations, Richland, Washington, 1981.
2. Arup, H. H. and G. Glatz, "An Evaluation of Corrosion of Sheer Steel Piling in Danish Harbors," 2nd International Congress on Metallic Corrosion, 1963, p. 767.
3. Barkman, L., "Conservation of Rusty Iron Objects by Hydrogen Reduction," Corrosion and Metal Artifacts - A Dialogue Between Conservators and Archeologists and Corrosion Scientists, National Bureau of Standards, Special Publication 479, 1977, p. 155.
4. Berge, Ph, C. Ribon, and P. Saint Paul, "Effects of Hydrogen on the Corrosion of Steel in High Temperature Water," Corrosion, Vol. 33, No. 5, 1977, p. 173-178.
5. Bhat, U. V., "Diffusion of H_2 in Steel," Indian Institute of metals - Transactions, Vol. ?, No. ?, 195?, p. 279-289.
6. Bloom, M. C. and M. B. Strauss, "Corrosion Mechanisms in the Reaction of Steel with Water and Oxygenated Solutions at Room Temperature and 316°C," J. Electrochemical Society, Vol. 107, No. 2, 1960, p. 73-79.
7. Braithwaite, I. W. and M. A. Nolecke, "Nuclear Waste Canister Corrosion Studies Pertinent to Geologic Isolation," Nuclear and Chemical Waste Management, Vol. 1, February 1980, pp. 37-50.
8. Braithwaite, I. W. and N. I. Magnani, "Corrosion Considerations for Nuclear Waste Isolation Canisters" in The Scientific Basis for Nuclear Waste Management, Vol. 2, Plenum Press, New York, 1979, p. 283-287.
9. Bureau of Reclamation, Corrosion of Some Ferrous Metals in Soil with Emphasis on Mild Steel and Grey and Ductile Cast Irons, U.S. Department of Interior, Washington, D.C., 1965.
10. Butler, G. and H. C. K. Ison, "Some Factors Influencing the Aqueous Corrosion of Ferrous Materials at Elevated Temperatures," 1st International Congress on Metallic Corrosion, 1961, p. 409-416.
11. BWIP Project View Graph Presentation for NRC Review Team, Richland, Washington, June 9, 1982.
12. Byalobzhesky, A. V., "General Regularities of Corrosion of Metals Under Radioactive Irradiation," 3rd International Congress on Metallic Corrosion, Vol. 4, 1966, pp. 287-293.
13. Carter, P. P., Personal Communication, 1982.

14. Charlot, L. A. and R. E. Westerman, Corrosion Resistance of Cast Irons and Titanium Alloys as Reference Engineered Metal Barriers for Use in Basalt Geologic Storage: A Literature Assesment, PNL-3569, Pacific Northwest Labs, Richland, Washington, 1981.
15. Cramer, S. D. and I. P. Carter, "Corrosion in Geothermal Brines of the Salton Sea Known Geothermal Resource Area" Geothermal Sealing and Corrosion, ASTM Technical Publication 717, Philadelphia, Pennsylvania, 1979, p. 113-141.
16. Dresselaers, I., F. Casteels, H. Tas "Corrosion of Construction Materials in Clay Environments" SCK/CEN Studiecentrum voor Kernenergie, Boeretang 200, B-2400 Belgium, (undated).
17. Effertz, P. H., "Morphology and Composition of Magnetic Layers in Boiler Tubes Following Long Exposure," 5th International Congress on Metallic Corrosion, 1972, p. 920-924.
18. Evans, U. R., The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications, New York: St. Martin's Press, Inc., 1960, p. 270, 439.
19. Feigenbaum, C., L. Gal-Or, and I. Yahalom, "Scale Protection Criterion in Natural Waters," Corrosion, Vol. 34, No. 4, 1978, p. 133-137.
20. Fujita, N. M. Akiyama, and T. Tamura, "Stress Corrosion Cracking of Sensitized Type 304 Stainless Steel in High Temperature Water Under Gamma Ray Irradiation," Corrosion, Vol. 37, No. 6, 1981, p. 335-341.
21. Gadiyar, H. S. and N. S. D. Elayathu, "Corrosion and Magnetite Growth on Carbon Steels in Water at 310°C - Effect of Dissolved O₂, pH and EDTA addition," Corrosion, Volume 36, No. 6, 1980, p. 306-312.
22. Galvele, J. R., "Passivity of Metals" R.P. Frankenthal and J. Kruger Eds, The Electrochemical Society, Princeton, NJ, 1978, p. 285.
23. Gause, E. P., L. G. Strang and D. R. Dougherty, Characterization of the Radioactive Large Quantity Waste Package of the Union Carbide Corporation, BNL-NUREG-30247R, Brookhaven National Laboratory, Upton, New York, 1982.
24. Glass, R. S., Effects of Radiation on the Chemical Environment Surrounding Waste Canisters in Proposed Repository Sites and Effects on the Corrosion Process, SAND81-1677, Sandia National Laboratories, Albuquerque, New Mexico, 1981, pp. 4-30.
25. Gutzeit, I. and I. R. Thyngenson, Jr., "Effect of Moisture on Decarborization and Fissuring of Steel by Hydrogen and Elevated Temperatures and Pressures," Corrosion, Vol. 23, No. 10, 1967, p. 318-325.
26. Hudson, J. C. and K. O. Watkins, Tests on the Corrosion of Buried Cast Iron and Mild Steel Pipes, Brittish Iron & Steel Research Association, London, 1968.

27. Huijbregts, W. M. M., A. Snel, and N. V. Kema, "Protection Effectiveness of Magnetic Layer in Relation to Boiler Corrosion," 5th International Congress on Metallic Corrosion, 1972, p. 857-865.
28. Hunter, I. B., H. F. McCononry and R. F. Weston, "Environmental pH as a Factor in Control of Anaerobic Bacterial Corrosion," Corrosion, Vol. 4, No. 12, 1948, p. 567-580.
29. Iverson, W. P., "Biological Corrosion" in Advances in Corrosion Science and Technology, Vol. 2, Ed: Fontana and Staehke Plenum Press New York, 1972, p. 14-42.
30. Johnson, A. B. and B. Francis, Durability of Metals From Archeological Objects, Metal Meteorites and Native Metals, PNL-3198, Pacific Northwest Laboratory, Richland, Washington, 1980.
31. Kruger, J. and K. Hardman, Current Understanding of Pitting and Crevice Corrosion and its Application to Test Methods for Determining the Susceptibility to Such Corrosion of Nuclear Waste Metallic Containers, National Bureau of Standards, Department of Commerce NBSIR-82-2497, 1982.
32. Latanision, Ronald, Private Communication, 1982.
33. Linnenbom, V. I., "The Reaction between Iron and Water in the Absence of Oxygen," Journal of the Electrochemical Society, Vol. 105, No. 6, 1950, p. 322-324.
34. 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.
35. Logan, K. H., Underground Corrosion, National Bureau of Standards, Circular C450, Washington, D.C. 1945.
36. MacDonald, D. D., B. C. Syrett, and S. S. Wing, "The Use of Potential pH Diagrams for the Interpretation of Corrosion Phenomena in High Salinity Geothermal Brines," Corrosion, Vol. 35, No. 1, 1979, pp. 1-11.
37. Mears, R. B. and U. R. Evans, Trans. Faraday Society, Vol. 31, 1935, p. 527.
38. Metals Handbook Vol. 1, Properties and Selection of Metals, 8th ed., American Society for Metals, 1961.
39. Molecke, M. A., I. A. Ryppen and R. B. Diegle, Materials for High Level Waste Canister/Overpacks in Salt in Basalt, AESD-TME-3113 Westinghouse Electric Corporation, Pittsburgh, Pennsylvania, 1981.
40. Molecke, M. A. et al., Sandia High Level Waste Canister/Overpack Studies Applicable for a Salt Repository, SAND81-1585, Sandia National Laboratories, Albuquerque, New Mexico, 1981.

41. Newby, D. et al., Waste Package Designs for Diposal of Nuclear Waste in Tuff, AESD-TME-3138, Westinghouse Electric Corporation, Pittsburg Pennsylvania, 1982.
42. Newby D. et al., Engineered Waste Package Conceptual Design Defense High-Level Waste (Form 1), Commerical High Level Waste (Form 1) and Spent Fuel (Form 2) Disposal in Basalt, AESD-TME-3113 Westinghouse Electric Corporation, Pittsburg, Pennsylvania, 1981.
43. Ogura, K. and Ohama, T., "Pit Formation in the Cathodic Polarization of Passive Iron II Effects of Anions" Corrosion, Vol. 37, No. 10, 1981, p. 569-574.
44. Oldfield, J. W. and W. H. Sutton, Journal of British Corrosion Vol. 13, 1978, p. 13.
45. Olsen, E. and W. Szybalski, "Aerobic Microbial Corrosion of Water Pipes," Corrosion, Vol. 16, No. 12, 1949, p. 405-414.
46. Parking, R. N., "Stress Corrosion Cracking of Low-Strength Ferritic Steels," The Theory of Stress in Alloys, NATO Brussells, 1971.
47. Piccinini, R., M. Marek, A. J. E. Pourbaix and R. F. Hochman, "A Study of Simulated Stress Corrosion Crack Tip Electrochemical Reactions." Localized Corrosion, Williamsburg, VA., 1971, pp. 179-183.
48. Potter, E. C., "Oxidation of Steel in Hot Aqueous Conditions and Its Significance in Steam Boiler Technology," 3rd International Congress on Metallic Corrosion, Vol. 4, 1966, p. 211-218.
49. Potter, E. C. and F. M. W. Mann, "Oxidation of Mild Steel in High-Temperture Aqueous Systems," 1st International Congress on Metallic Corrosion, 1960, p. 417-429.
50. Pourbaix, M., Lectures on Electrochemical Corrosion, Plenum Press, New York, 1973, pp. 17, 223-225, 269-280.
51. Reinhart, F., "First Results - Deep Ocean Corrosion Geomaine Technology, September, 1965, v295 - v306.
52. Romanoff M., "Performance of Ductile Iron Pipe in Soils" Journal of the American Water Works Association, Vol. 60, No. 6, 1968, pp. 645-655.
53. Romanoff, M., Underground Corrosion, National Bureau of Standards, Circular 579, April 1957.
54. Rosenfeld J. L. and I. S. Danilov, Corrosion Science, Vol. 17, 1967, p. 129.
55. Shannon, D. W., "Corrosion of Iron-Base Alloys versus Alternative Materials in Geothermal Brines," PNL-2456, Battelle, Richland, Washington, 1977, p. 15.

56. Smith, M. I., et al., Engineered Barrier Development For A Nuclear Waste Repository in Basalt: An Integration of Current Knowledge, RHO-BWI-ST-7, Rockwell Hanford Operations, Richland, Washington, 1987.
57. Southwell, C. R. and A. L. Alexander, "Corrosion of Metals in Aqueous Environments over Extended Periods," Proceedings of the 3rd Internal Corrosion Conference, April 1969, pp. 19A.1-15.
58. Southwell, C. R., B. W. Fageson, and A. C. Alexander, "Corrosion of Metals in Tropical Environments, Part 4 - Wrought Iron," Corrosion, Vol. 16, No. 11, 1960, p. 512t.
59. Stepanov, I. A. and B. V. Strockan, "Corrosion of Metals in Seawater under Heat Transfer Conditions," 3rd International Congress on Metallic Corrosion, Vol. 3, 1966, p. 52-59.
60. Townsend, H.E., H.J. Cleary and L. Allegra "Breakdown of Oxide Films on Steel exposed to Chloride Solutions," Corrosion, Vol. 37, No. 7, 1981, p. 384-391.
61. Tylecote, R. F., "The Adherence of Oxide Films on Metals, A Review of Information," Journal of the Iron Steel Institute, August, 1960, p. 380-385.
62. White, L. A., M. J. Bell and D. M. Rohrer, "Regulation of Geologic Repositories for the Disposal of High-Level Radioactive Wastes" in The Scientific Basis for Nuclear Waste Management, Vol. 2, Plenum Press, New York, 1979, p. 5-19.
63. Yasuda, M., M. Okada and F. Hine, "Corrosion of Carbon Steel in Hot NaOH Solutions under Heat Transfer Conditions," Corrosion, Vol. 3, No. 5, 1982, p. 256-261.

**Table #1 Comparison of General and Pitting
Corrosion Rates**

Material	Soil or Solution:	Synthetic Basalt	Fresh Water	L10H	L10H	1% NaCl	Brine "A"*	Sagamoor HA Loam	Hanford Loam
Carbon Steel (rate in mm/yr)	Oxygen:	50ppb-1 ppm	OXIC	<0.05 ppm	3.5 ppm	<0.01 ppm	~30 ppbO ₂	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	Southwell & Alexander 1970	Gadiyar & Elaythu 1980		Shannon 1977	Braithwaite Molecke 1980	Romanoff 1958	Romanoff 1957
	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.8-7 (ductile iron b.22-8 ductile iron + .73 Cu c.142-12 grey + .68 Cr 1.34 Cu d.1663 - grey iron e.136-4 grey iron + 3.05 Hf	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 ID 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 Hot Solution	

Table 2 Corrosion of carbon steel in steam and air
(Metals Handbook Vol. 1, 1961)

Corrosive Medium	Temp. °C	Alloy	Penetration Depth after 10,000 hrs. (14 months) mm x 10 ³	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
(Metals Handbook Vol. 1, 1961)

Materials: Cast Iron & Carbon Steel
Environment: Anoxic Brine

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

*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 (Newby 1982)

<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 ₂ O	250	Parabolic	.38	1.90
13% NaOH	250	Linear	.38	1.90
Neutral H ₂ O	250	Linear	.66	3.30
Soil	Ambient	Linear	.57	2.55

Table 5 The effects of radiation on uniform corrosion of 1018 steel (Molecke, SAND 81-1585)

T = 90°C

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

*Estimated from data given by Braithwaite and Molecke (Braithwaite 1980), assuming linear kinetics between data points at 70°C and 250°C.

Table 6 Comparison of Oxide Attributes (After

<u>Composition</u>	<u>Mineral Name</u>	<u>Electrical Resistivity</u>	<u>Density gm/cm²</u>	<u>Thermal Behavior</u>	<u>Chemical Stability</u>
Fe(OH)_2	----	Insulator	3.40	Decomposes at 100°C to magnetite	<ul style="list-style-type: none"> • Stable only in absence of O_2. • Highly soluble in water.
Fe_3O_4	Magnetite	Electrical Conductor	5.20	Stable to 1597°C	<ul style="list-style-type: none"> • Insoluble in high temperature water. • May be partially reduced by hydrogen to ferrous hydroxide.
$\gamma - \text{Fe}_2\text{O}_3$	Maghemite	Semiconductor to insulator	4.88	Transforms to hematite above 250°C	<ul style="list-style-type: none"> • Water causes conversion to hematite at lower temperature.
$\alpha - \text{Fe}_2\text{O}_3$	Hematite	Insulator	5.25	Decomposes to magnetite at 1459°C and 1 atm	
$\delta - \text{FeOOH}$	Lepidocrocite	Insulator	3.97	Dehydrates to maghemite above 200°C	<ul style="list-style-type: none"> • Water causes conversion to maghemite at lower temperatures.
$\alpha - \text{FeOOH}$	Goethite	Insulator	4.20	Dehydrates to hematite above 200°C	<ul style="list-style-type: none"> • Water causes conversion to hematite at lower temperatures.

Bloom, et al and M.B. Strauss ; Petten, E.C.)

Table 16 Comparison of Oxide Attributes (After

<u>Composition</u>	<u>Mineral Name</u>	<u>Electrical Resistivity</u>	<u>Density gm/cm³</u>	<u>Thermal Behavior</u>	<u>Chemical Stability</u>
Fe(OH)_2	----	Insulator	3.40	Decomposes at 100°C to magnetite	<ul style="list-style-type: none"> • Stable only in absence of O_2. • Highly soluble in water.
Fe_3O_4	Magnetite	Electrical Conductor	5.20	Stable to 1597°C	<ul style="list-style-type: none"> • Insoluble in high temperature water. • May be partially reduced by hydrogen to ferrous hydroxide.
$\gamma - \text{Fe}_2\text{O}_3$	Maghemite	Semiconductor to insulator	4.88	Transforms to hematite above 250°C	<ul style="list-style-type: none"> • Water causes conversion to hematite at lower temperature.
$\alpha - \text{Fe}_2\text{O}_3$	Hematite	Insulator	5.25	Decomposes to magnetite at 1459°C and 1 atm	
$\delta - \text{FeOOH}$	Lepidocrocite	Insulator	3.97	Dehydrates to maghemite above 200°C	<ul style="list-style-type: none"> • Water causes conversion to maghemite at lower temperatures.
$\alpha - \text{FeOOH}$	Goethite	Insulator	4.20	Dehydrates to hematite above 200°C	<ul style="list-style-type: none"> • Water causes conversion to hematite at lower temperatures.

Table 7 Basalt groundwater (Newby D et al., AESD-TMT-3113, 1981)

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

Table 8 Corrosion of weld and nonweld specimen
in salton sea brine in mm/yr (Galvele, 1978)

Temperature: 232°C ppm Cl⁻: 155,000 pH: 6.1 at 25°C

Alloy/Filler Alloy	Nonweld deaerated	Weld	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

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

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 _h (VOLTS)	PRESSURE (BARS)
OPERATING PERIOD	59	9.6	+0.51	1
THERMAL PERIOD	100	8.7	-0.50	114
	150	7.9	-0.52	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	-0.43	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.

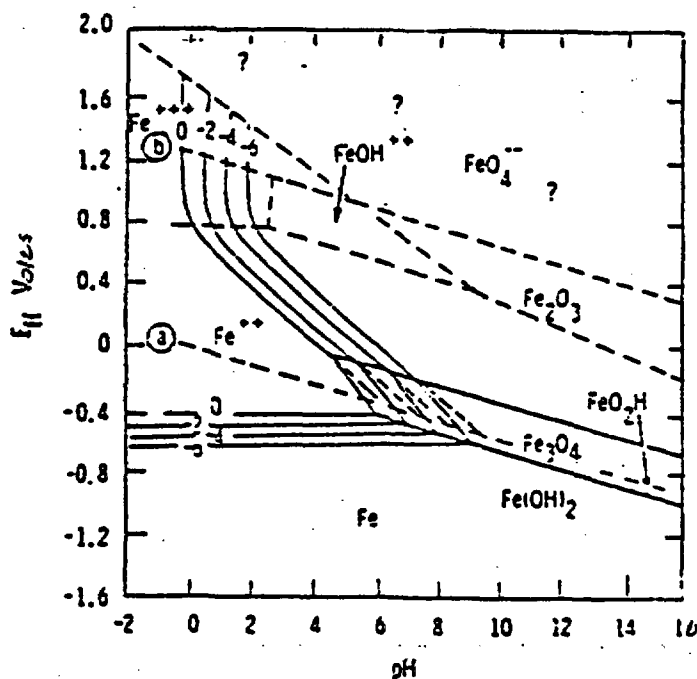


Figure 1 Pourbaix diagram for Fe-H₂O-25°C (Pourbaix 1973)

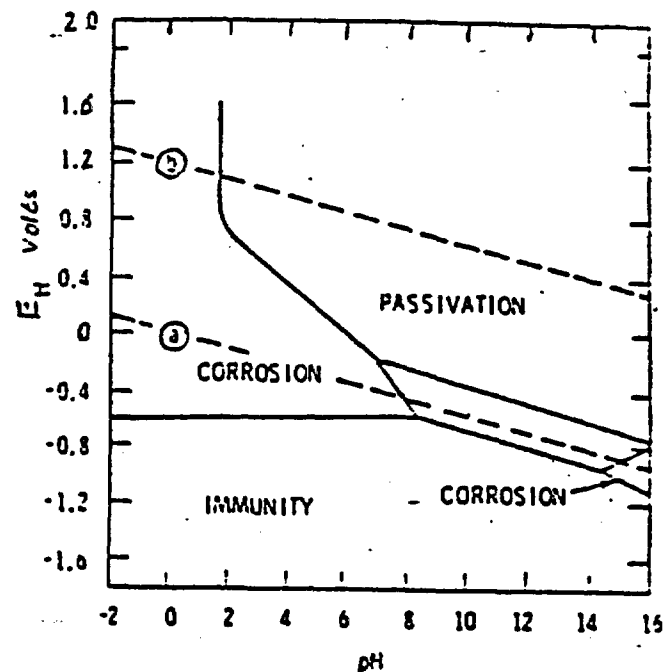


Figure 2 Passivation Areas for the Fe-H₂O System (Pourbaix 1973)

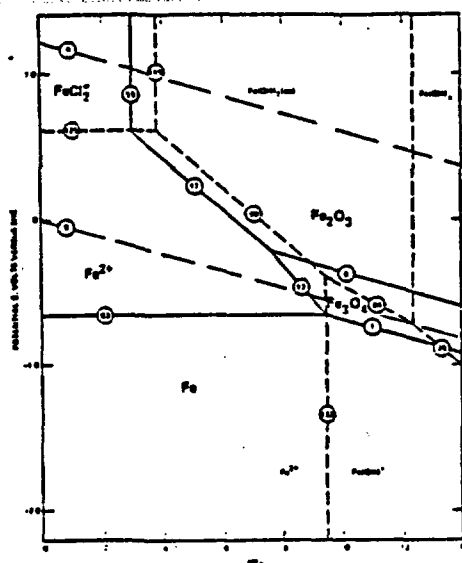


Figure 3 Potential pH diagram for iron in high salinity brine at 25 C. (MacDonald, Syrett and Wing)

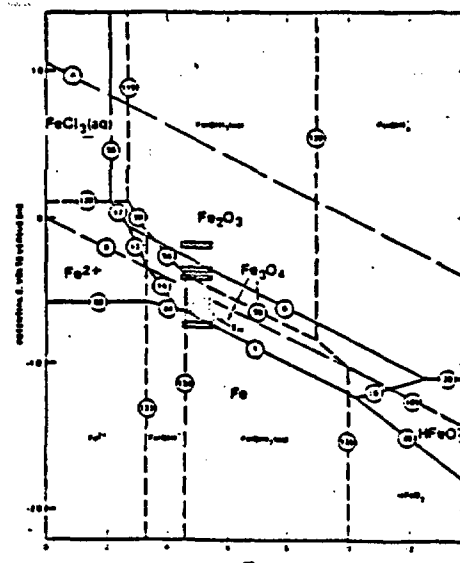


Figure 4 Potential pH diagram for iron in high salinity brine at 250 C. (MacDonald, Syrett and Wing)

- a) represents a lower stability line for water $\text{H}_2 \leftarrow 2\text{H}^+ + 2\text{e}^-$
- b) represents an upper stability line for water $\text{H}_2\text{O} \rightarrow 1/2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$

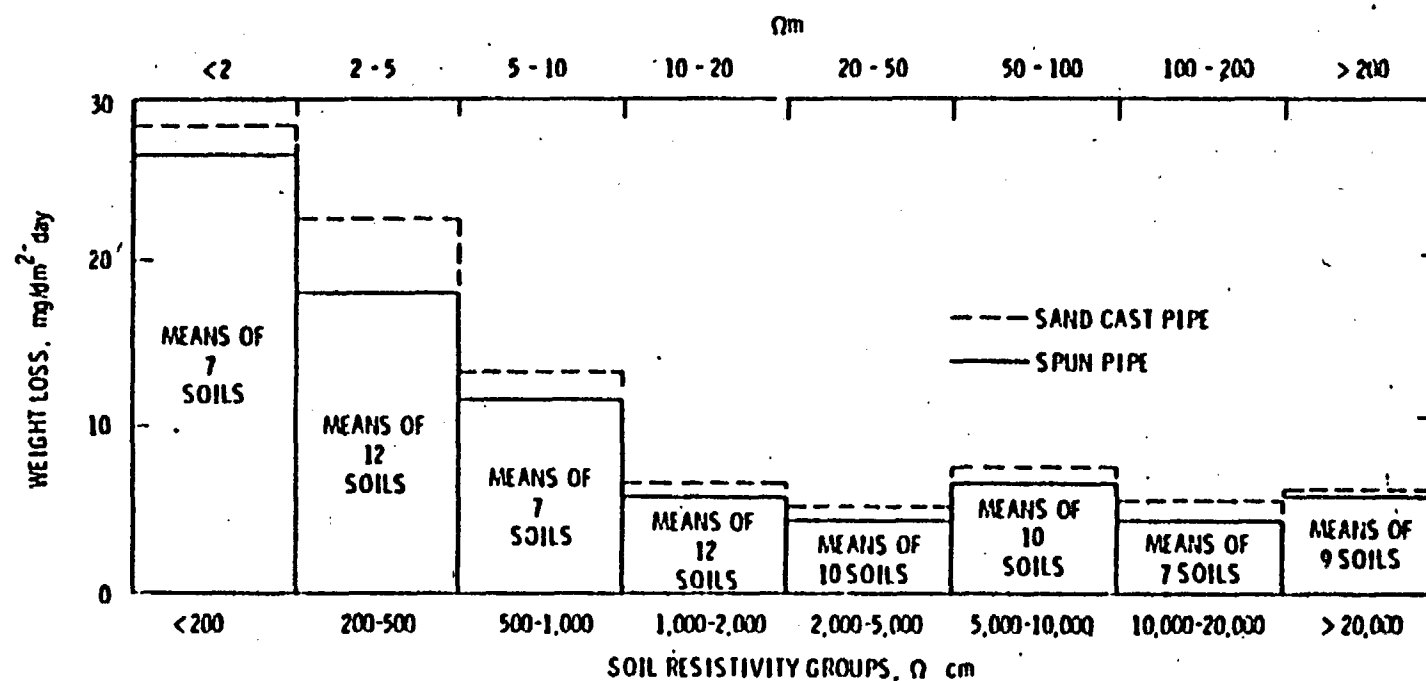
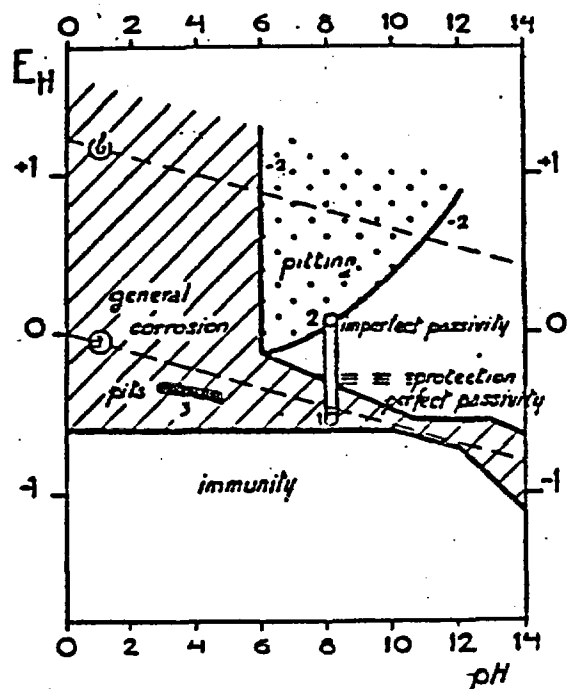


FIGURE 5. Corrosion of Gray Iron in Soils of Differing Resistivity

Figure 6 Pourbaix diagram for iron with 355 ppm Cl^-

At pH 8 this can be interpreted as: (Pourbaix 1973)

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



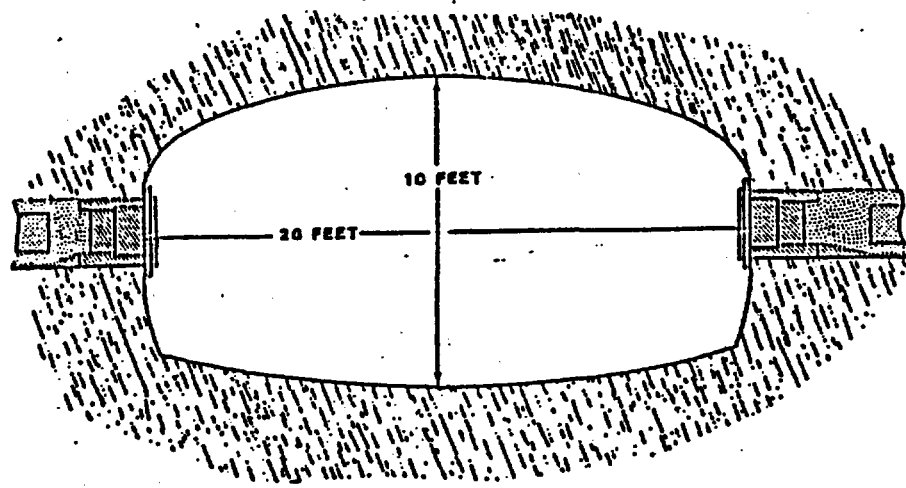


Figure 7 Dimensions of a repository draft

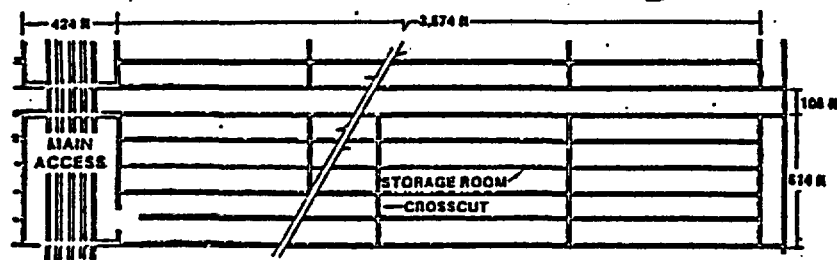


Figure 8 Typical crosssection of repository

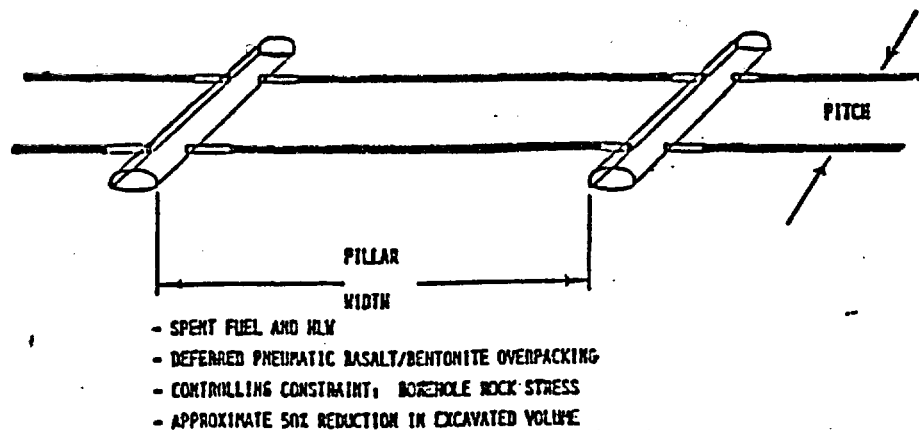


Figure 9 Dimensions of boreholes between drifts

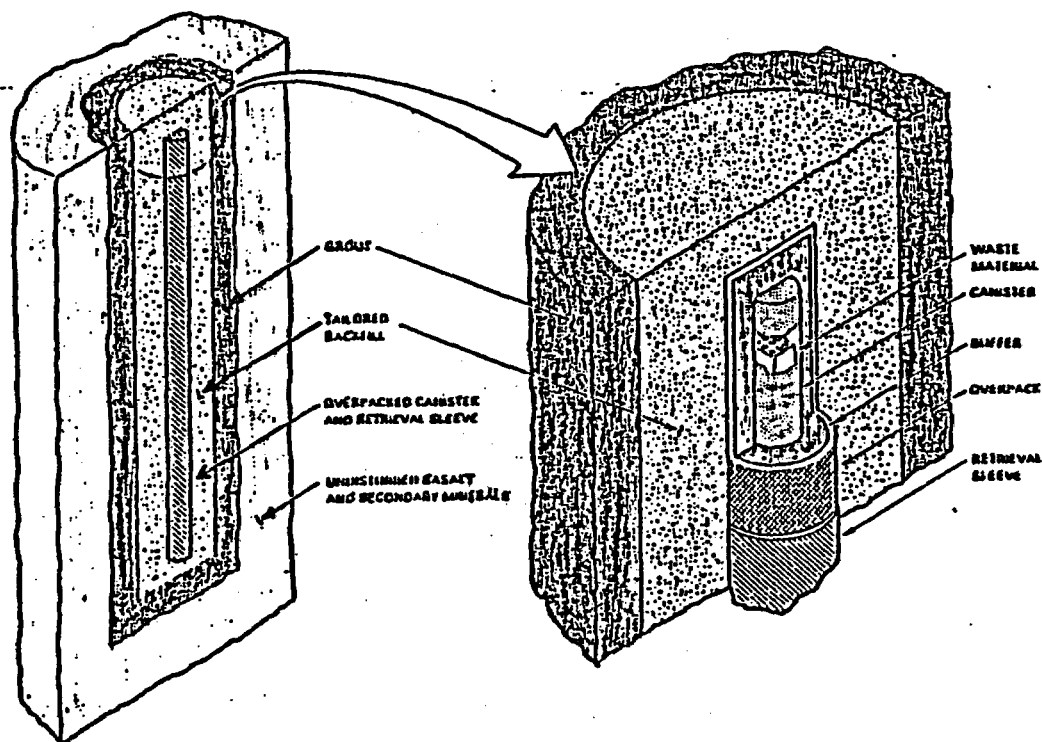


Figure 10 Borehole design

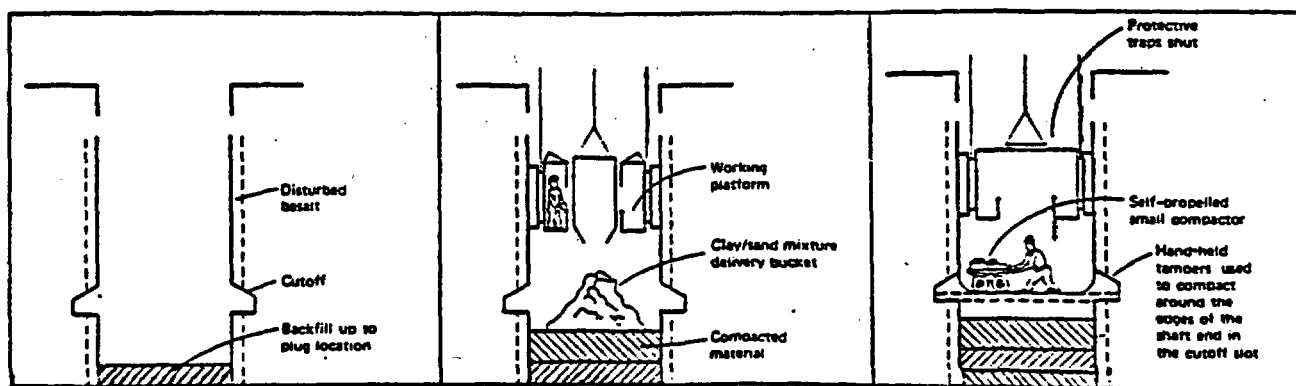


Figure 11 Backfilling Main Shaft of Repository

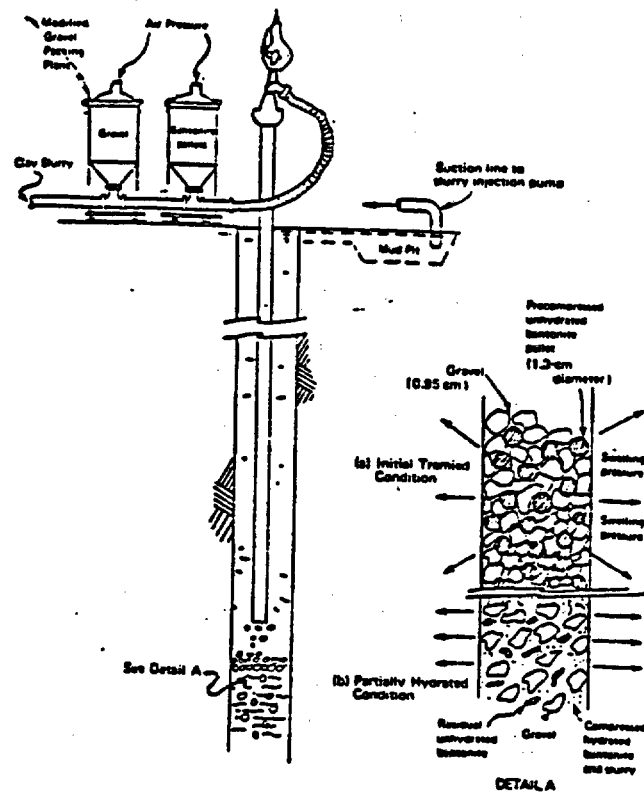


Figure 12 Backfilling of borehole

note: This design assumes vertical borehole

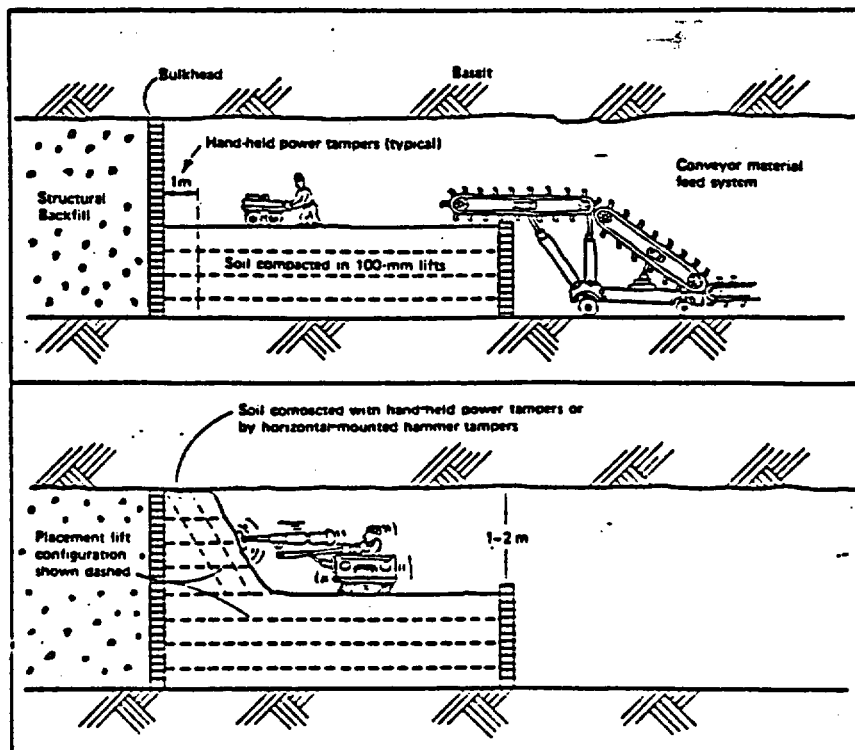


Figure 13 Backfilling a large drift

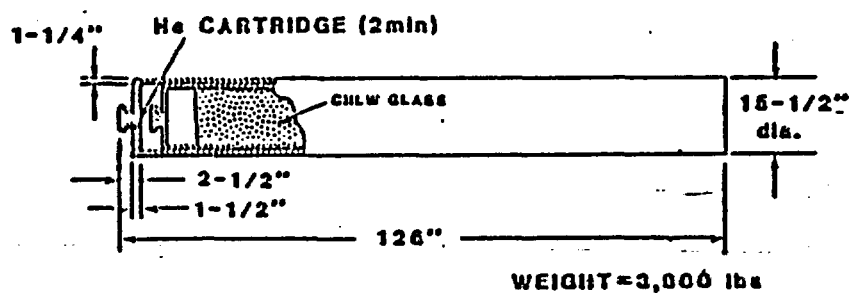
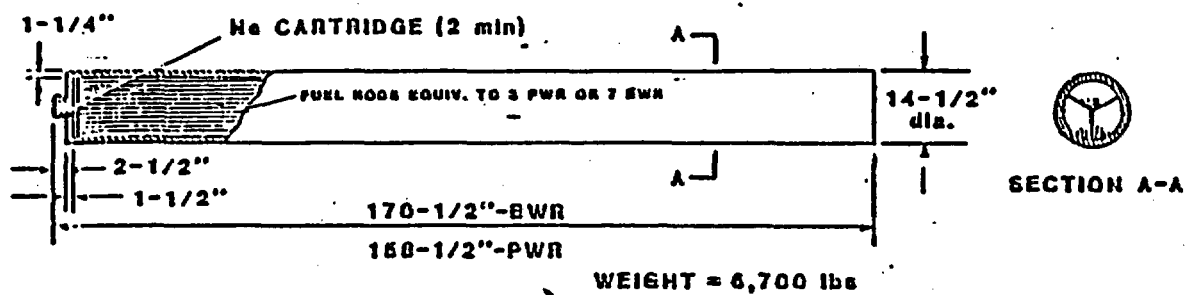


Figure 14 Canister construction with dimensions

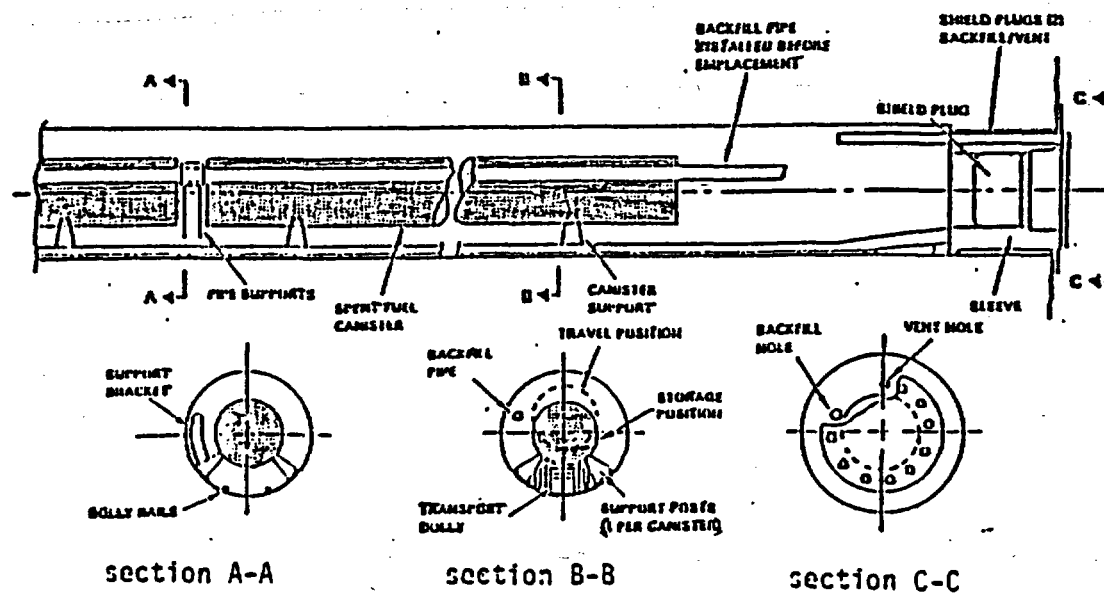


Figure 15 Canister emplacement

APPENDIX Q

DEGRADATION MECHANISMS OF BOROSILICATE GLASS

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DEGRADATION MECHANISMS OF BOROSILICATE GLASS

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.

The purpose of this section 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. 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.

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 a likely condition to be encountered in actual repository environments.

2.1 Kinetic Law

There is general consensus that in a static condition stage 1, dealcalization 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:

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

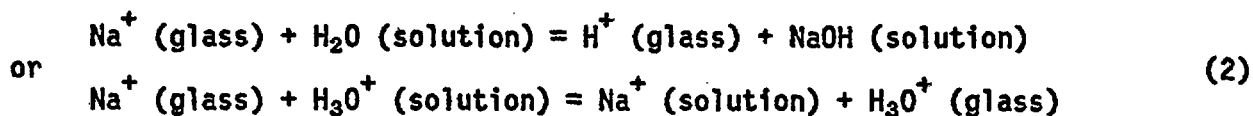
where a and b are appropriate constants. No comprehensive mechanistic studies are available at the present time to explain this relation. The square root indicates a diffusion controlled reaction and the linear relation reflects an interface controlled reaction. The relation is more or less empirical 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 ' at long times and high temperatures. Examples include the work done on glass powders (Holland, L. 1964), on alkali-oxide silica and soda-lime silica glasses (Douglas, R.W., 1967; El-Shamy, T.M., 1972), and on PNL 72-68 glass (Hench, L.L., 1978).

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.

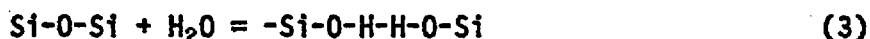
The formulation of leach kinetics through the use of empirical or semi-empirical equations is based on several assumptions such as homogeneous leaching, the preservation of leachant composition, surface area and mechanical integrity. In real situations, these factors should be incorporated into the formulations.

2.2 Reaction Mechanism and Kinetic Models

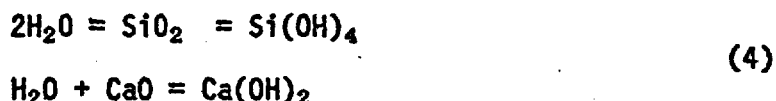
At least three different stages are involved in the reaction of water with a silicate glass containing alkali ions: The first is ion exchange of hydronium (H_3O^+) or hydrogen ions from the water with alkali ions in the glass; the second is the partial hydration of the silicon-oxygen network of the glass; 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 (Doremus, R.H. 1973; Doremus, R.H., 1979) 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 (Doremus, R.H., 1979):



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 (Doremus, R.H., 1979):



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

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 (Hench, L.L., 1977; Hench, L.L., 1975) 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 (Paul, A., 1977) 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 (SiO_2 , ZnO , PbO , Al_2O_3 , 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 (Doremus, R.H., 1979) 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. 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. 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., (Godbee, H.W., 1980; ORNL-TM-4333) 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 (Ewest, E., 1979) for more ideal situations, and by Machiels, (Machiels, A.J., 1980a; Machiels, A.J., 1980b) 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 (Barkatt, A., 1978; Macedo, P.B., 1979; Macedo, P.B., 1980) and at Brookhaven National Laboratory (Ahn, T.M., 1980) 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.

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. (Hench, L.L., 1980) 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 Na_2O and K_2O together serves to lower the rate of surface dealcalization).

The influence of the salt compounds on improved durability has been investigated, indicating some of the effects of solution ions on the durability of glass (Hench, L.L., 1978; Hench, L.L., 1977). The influence of the salt compounds on leaching are in decreasing order: CaCl_2 , ZnCl_2 , AlCl_3 . Two extremes, Ca^{2+} and Al^{3+} , will be described as follows: 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 Al^{3+} ions in concentrations up to 25 ppm, glass dissolution increased due to a more rapid increase in dealcalization and resultant solution pH. This is due to insufficient Al^{3+} ions to passivate active surface sites and incomplete formation of stable aluminosilicate surface complexes. At concentrations greater than 25 ppm Al^{3+} , the total dissolution of the glass is greatly reduced. Sufficient concentration of Al^{3+} in solution creates a dual protective film against extensive network dissolution. The rate of selective leaching or ion exchange within the glass is relatively unaffected by the presence of Al^{3+} in solution.

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 (the

reference waste form glasses are not low expansion glasses) 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 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 in the glass to increase silica dissolution. Hench (Hench, L.L., 1980) 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).

The addition of other constituents, such as lime, only slightly modified the typical shapes of the graphs. For more complicated glasses, such as borosilicate waste 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 which is a high silica glass) it leads to reduced alkaline durability. Similarly, in 0010 glass (a high silica and high lead) small amount of lead has little effect on durability, while in large 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 leach rates of U.K. borosilicate waste glass being pH dependent as shown in Figure 2.4 (Boult, K.A. 1979). It has been shown that leach rates are increased by low as well as high pH leachants. 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 2.5 (ONWI-212) and 2.6 (DPST-79-294).

Waste glasses usually contain less than 50 wt.% SiO_2 while commercial container glasses contain more than 70 wt.% SiO_2 . This accounts for the difference in behavior at lower pH (PNL-3802). At high pH, the trend of leach rates for waste glasses generally follows that of commercial glasses. In actual repository conditions, the unbuffered solution or groundwater that first contacts the waste would have little effect on the leach rate; however,

as the concentration level of the leached sodium builds up in the leachant the pH would increase and the increased pH would accelerate the leak rate.

2.3.3 Flow Rate

The replacement or flow of solutions has been reported as showing two opposite effects on the glass corrosion. In a leach test of K_2O-SiO_2 glass at $40^\circ C$ (El-Shamy, T.M., 1972), 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 (Maceclo, P.G., 1980). If the flow rate is high enough to keep the system from reaching 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 retarded (NUREG/CR-2333, vol. 4). At very high flow rates, the leach rates would be controlled by the pH of the medium and the stability of the dealkalinized layer. Taylor and Smith (Shand, E.B., 1958) reported a significant increase in weight loss under these erosive conditions.

Some leach data are available for borosilicate waste glass subjected to different flow rates. Leach rates on British waste glasses (Boult, K.A., 1979) were obtained using a Soxhlet apparatus, heating in static water, and exposed to flowing ($1 \times 10^{-8} \text{ m}^3/\text{sec}$) water. Duration of the tests was dependent on time sufficient to achieve a measurable weight loss. This varied from approximately one week at $100^\circ C$ 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 ^{238}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 effect on the leach rates as indicated by the above observations.

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 to $15^\circ C$ rise in temperature and the reaction rate increased by a factor of 10-100 for every $100^\circ C$ increase in temperature, depending on the composition of the glass and the type of alkali ion. Some workers (Paul, A., 1977) 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 $80^\circ C$, 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 (White, W.B., 1980). For PNL waste glass (Mendel, J.E., 1980) representative leach rates at 25°C are 1×10^{-6} to 1×10^{-5} g of glass/cm²-day. Representative leach rates at 40-50°C are 5×10^{-6} to 5×10^{-5} g of glass/cm²-day. White (White, W.B., 1980) 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 (300°C and 300 bars) reactions of waste glass.

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 shards to crystalline and non-crystalline products plus dissolved species in a two week period. The major products were (Cs, Na, Rb)₂(UO₂)₂(Si₂O₅) · 4H₂O (weeksite) and pyroxene-like phases (Na, Ca)(Fe, Zn, Ti)Si₂ (acmite, augites). High Na₂O and low SiO₂ may be responsible for the rapid alteration of the sample.

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 (Strathdee, G.G., 1980). Zincoilite 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 sub-liquidus 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 in glass begins to recrystallize under prolonged leach conditions. Barkatt (Barkatt, A., n.d.) 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 solution 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

Adams and his co-workers (Adams, P.G., 1978) have provided a generalized ternary description of complex commercial glasses composed on 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 2.7). 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.

The composition effect has been studied, qualitatively in most cases (Doremus, R.H., 1979; Hench, L.L., 1977; Paul, A., 1977; Barkett, A., 1978; Westsik, J.H., 1979; Strathdee, G.G., 1980) by considering whether the component: (1) is thermodynamically stable in a given pH-temperature range and whether it 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

- o SiO_2 : The stability of vitreous silica has been illustrated for a given pH range at room temperature. 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.
- o Al_2O_3 : The addition of Al_2O_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.
- o ZrO_2 : A small amount of ZrO_2 (about 2 weight percent) increases acid and alkaline durability. The hydrated ZrO_2 surface is stable at all conceivable pH ranges and offers a very high activation barrier for the diffusion of other ionic species.
- o TiO_2 : Similar to Al_2O_3 and ZrO_2 , TiO_2 is expected to increase chemical durability. However, no measurements of ionic mobilities are available.
- o P_2O_5 : An extensive investigation of corrosion reactions of an inert soda-lime-silica glass containing P_2O_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_2O_3

B_2O_3 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_2O_5 -containing glass. The extracted B_2O_3 acts to neutralize the alkali and reduce the solution pH. These effects combine to increase glass durability.

Network Modifier: R_2O

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_2O group is in the order is $Li_2O > Na_2O > K_2O$. Their role in the formation of a durable SiO_2 -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: RO

- o 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 $CaO-SiO_2$ -rich film reducing the surface dissolution rate. However at high temperatures, CaO greatly weakens the glass network.
- o 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.
- o 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.
- o 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 (Mellinger, G.B., 1979) centered on the effects of 26 oxides in a generic study of defense waste glass. Chemical durability was tested in acid and basic solutions and in distilled water at room temperature and at $99^\circ C$; percent weight loss was determined for each of the samples. Table 2.2 is a summary of the results which show a general agreement with the summary of each component described previously. In addition, the effects of U_3O_8 , MnO_2 , Fe_2O_3 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.

A PNL study (PNL-3060; PNL-3050-2) 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 2.8 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 2.9).

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.

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_2 rich) phase particles dispersed in the chemically less durable (e.g., $Na_2O-B_2O_3$ 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 microstructural type C described above.

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 (having a maximum depth of 20A), 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. (Skattula, W., 1958) for Pyrex-type glass have illustrated the phenomenon of decreased durability due to phase separation. Transitions in behavior between a discontinuous and 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 leading 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° 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 $Na_2O-B_2O_3-SiO_2$ have received the widest attention since this system is the basis of many commercial borosilicate glasses. A variety of sodium borosilicate glasses containing up to about 10% Na_2O and from about 10% to 70% B_2O_3 (balance: 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 boundary 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 (Tomozaawa, M., 1964) is commercial borosilicate glass with an interconnected microstructure having an excess Al_2O_3 concentration in the surface layer. Excess Al_2O_3 lowers the HF etch rate because of the lower extent of phase separation on the 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.

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, i.e., a silica-lithium glass (Hench, L. L., 1980) 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. (Hench, L. L., 1980) 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. (Wald, J. W., 1979.) 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. (Westsik, J. H., 1979.) The formation of a zinc-rich alteration zone was reported as being composed of mainly zincsilite under hydrothermal conditions in sodium zinc borosilicate glass. (Strathdee, G. G., 1980.) 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. 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 constraints, 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 has been observed for various (SA/V) ratios. (Hench, L. L., 1980.) It was shown that the increase of (SA/V) leads to a more rapid pH change. 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.

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. (Wald, J. W., 1979.) 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. (Shumitskaya, L. F., 1976.) 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 ^{244}Cm -doped waste borosilicate glass exhibited microfracturing with no accompanying measurable effect on leach rate. (Weber, W. J., 1980; PNL-3050-1.) Other groups have, however, considered the significance of cracking. (Barkatt, A., 1978; PNL-SA-7369.) Recently a more systematic simulation of cracking was performed by Perez, et al. (Perez, J. M., 1980.) 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. It should be noted that for most cases, the increased cracked area does not appear to result in a proportional increase in leach rates.

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.

Generally a more rapid reaction has been observed in the case of glass quenched with water compared to annealed glass. (Doremus, R.H., 1979; Morey, G. W., 1954.) This result can be understood from the higher ionic mobility in the quenched glass which has a lower density and a more open structure. (Morey, G.W., 1954; Charles, R.J., 1962.) However, the quantity of the enhancement is usually not significant, being at most a few percent. 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. (Adams, P. B., 1978.)

Glass homogeneity also affects leach rates. Inhomogeneity in this case mainly includes the quantity of undissolved constituents. Studies of 76-68 glass with several difference thermal histories have shown that the best leach resistance was obtained from the glass exhibiting the best homogeneity. (Hench, L. L., 1980.) 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. (Sanders, D. M., 1973.) 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 Weathering

Even though a water solution may be absent, chemical reaction can occur in the presence of water vapor. Static and cyclic humidity as well as wet-dry cycles 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.

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. (Adams, P. B., 1979.) At the Conasauga test site (Tennessee; shale) PNL 75-25 borosilicate glass, subjected to alternating wet-dry cycles, exhibited a 20µm-thick layer showing network cracks and nonuniform penetration of corrosion into the underlying unaltered bulk glass. (ONWI-62.) 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.

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. 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 microstructuring and surface flaws require additional experimental treatment.

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 high stressed region near the crack tip. The general characteristics of static fatigue are as follows:

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

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 may be found in the literature. (NUREG/CR-2333, Vol. 1.)

In waste glass, alpha, beta, gamma-rays, and transmutation effects are expected to exist. (NUREG/CR-2333, Vol. 4.) Recently, Walker, et al. (Walker, D.D., 1981.) reported on a preliminary study involving borosilicate glass leaching during ^{60}Co gamma, ^{244}Cm alpha, and ^{90}Sr beta radiation. The 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 (Weber, W. J., 1980b) seem to indicate that the effect may not be significant. Indirect effects involving differential swelling and compaction, which lead to microfracturing, have been observed in partially devitrified glass by that was subjected to alpha and gamma radiation. The concomitant increase of surface area will enhance the leach rate significantly. 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 on this topic.

5 CONCLUSIONS

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.

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. With respect to radiation effects, radiolysis, radiation-induced cracking and pH change require further investigation.

REFERENCES

1. Adams, P. B., and D. L. Evans, "Chemical Durability of Borate Glasses", In L. D. Pye, V. D. Frechette, and N. J. Kveidl, eds., Borate-Glasses: Structure, Properties, Applications, New York, Plenum, 1978.
2. Adams, P. B., "Chemistry of Nuclear Waste Glass Reaction = Problems and Potential of Prediction," in G. J. McCarthy, Ed., Scientific Basis for Nuclear Waste Management, Vol. 1, New York, Plenum, 1979.
3. Ahn, T. M., R. Dayal, and K. J. Swyler, "Chemical Durability and Structural Stability of Molecular Stuffed Glass - An Evaluation," BNL Memorandum, 1980.
4. Barkatt, A., "Stability of Fixation Solids for High-Level Radioactive Wastes", in High-Level Radioactive Solid Waste Forms, NUREG/CP-0005, 1978.
5. Barkatt, A., "Static and Dynamic Tests for the Chemical Durability of Nuclear Waste Glass," in press.
6. Boulton, K. A., "The Leaching of Radioactive Waste Storage Glasses," in Ceramics in Nuclear Waste Management, CONF-790420, 1979.
7. Charles, R. J., Journal of the American Ceramic Society, **45**, 105, 1962.
8. Doremus, R. H., "Chemical Durability in Glass", in M. Tomozawa and R. H. Doremus, Eds., Treatise on Materials Science and Technology, Vol. 17, New York, Academic Press, 1979.
9. Doremus, R. H., Glass Science, New York, Wiley Publications, 1973.
10. Douglas, R. W., and T. M. El-Shamy. Journal of the American Ceramic Society, **50** (1), 1967.
11. DPST-79-294, "Glass as a Matrix for SRP High-Level Defense Waste", Savannah River Laboratory, 1980.
12. El-Shamy, T. M., and R. W. Douglas, Glass Technology, **13**, 77, 1972.
13. Ewest, E., "Calculations of Radioactivity Release Due to Leaching of Vitrified HLW," in G. J. McCarthy, Ed., Scientific Basis for Nuclear Waste Management, Vol. 1, New York, Plenum Press, 1979.
14. Godbee, H. W., et al., Nuclear and Chemical Waste Management, **1**, 29, 1980.
15. Hench, L. L., D. E. Clark, and E. L. Yen-Bower, Nuclear and Chemical Waste Management **1**, 59, 1980.
16. Hench, L. L., D. E. Clark, and E. L. Yen-Bower, "Surface Leaching of Glasses and Glass Ceramics," in High-Level Radioactive Solid Waste Forms, NUREG/CP-0005, 1978.

17. Hench, L. L., "Physical Chemistry of Glass Surfaces," in Proceedings of the XIth International Congress on Glass, 1977.
18. Hench, L. L., Journal of Non-Crystalline Solids, 19 (27), 1975.
19. Holland, L., "Surface Chemistry and Corrosion of Glass", in The Properties of Glass Surfaces, New York, Wiley Publications, 1964.
20. Macedo, P. B., et al., "Porous Glass Matrix Method for Encapsulating High-Level Nuclear Wastes", in Ceramics in Nuclear Waste Management, CONF-790420, 1979.
21. Macedo, P. B., A. Barkatt, and J. H. Simmons, "A Flow Model for the Kinetics of Dissolution of Nuclear Waste Glasses", Proceedings of ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, 1980.
22. Machiels, A. J., "Prediction of Initial Leach Rates of Glass Waste Forms," in Proceedings of the International Conference on World Nuclear Energy, Transactions of the American Nuclear Society, 1980a.
23. Machiels, A. J., "Short-Term Leaching Behavior of Waste Forms," in Proceedings, Workshop on Alternative Nuclear Waste Forms and Interactions in Geologic Media, Gatlinburg, Tennessee, 1980b.
24. Mellinger, G. B., and L. A. Chick, "Effects of Composition on Waste Glass Properties," in Ceramics in Nuclear Waste Management, CONF-790420, 1979.
25. Mendel, J. E., Nuclear and Chemical Waste Management, 1 (17), 1980.
26. Morey, G. W., The Properties of Glass, New York, Reinhold, 1954.
27. Nordberg, M. E., "Chemical Durability", Corning Glass Works, unpublished manuscript.
28. NUREG/CR-2333, "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 1 - Waste Package Overview, Brookhaven National Laboratory, 1982.
29. NUREG/CR-2333, "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 4 - Test Development Review, "Brookhaven National Laboratory, 1982.
30. ONWI-162, "Proceedings of the National Waste Terminal Storage Program Information Meeting, October 31-November 1," 1979.
31. ONWI-212, "Proceedings of the 1980 National Waste Terminal Storage Program Information Meeting", 1980.
32. ORNL-TM-4333, "Assessment of the Loss of Radioactive Isotopes From Waste Solids to the Environment. Part 1. Background and Theory," Oak Ridge National Laboratory, 1974.
33. Paul, A., Journal of Materials Science, 12, 2246, 1977.

34. Perez, J. M., and J. H. Westsik, "Effects of Cracks on Glass-Leaching," Proceedings of ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, 1980.
35. PNL-SA-7369, "Stresses and Cracking in HLW Glass", Pacific Northwest Laboratory, 1978.
36. PNL-3050-1, "Quarterly Progress Report - Research and Development Activities - HLW Immobilization Program, January through March 1979," Pacific Northwest Laboratory, 1979.
37. PNL-3050-2, "Quarterly Progress Report - Research and Development Activities - HLW Immobilization Program, April 1 through June 30, 1979," Pacific Northwest Laboratory, 1979.
38. PNL-3060, "Annual Report on the Development and Characterization of Solidified Forms for HLW," Pacific Northwest Laboratory, 1979.
39. PNL-3802, "MCC, A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms," Pacific Northwest Laboratories, 1981.
40. Sanders, D. M., and L. L. Hench, Ceramic Bulletin, 52, 666, 1973.
41. Shand, E. B., Glass Engineering Handbook, New York, McGraw-Hill, 1958.
42. Shumitskaya, L. F., Izvestiya Akademii Nauk USSR, Vol. 12, 88, 1976.
43. Skattula, W., W. Vogel, and H. Wessel, Silikattechnik Vol. 9, 323, 1958.
44. Shathdee, G. G., N. S. McIntyre, and P. Taylor, "Development of Alumino - Silicate and Borosilicate Glasses or Matrices for CANDU HLW," Proceedings, Workshop on Alternative Nuclear Waste Forms and Interactions in Geologic Media, Gatlinburg, Tennessee, 1980.
45. Tomozawa, M., "Phase Separation in Glass" in The Properties of Glass Surfaces, New York, Wiley Publications, 1964.
46. Wald, J. W., and J. H. Westsik, "Devitrification and Leaching Effects in HLW Glass - Comparison of Simulated and Fully Radioactive Waste Glass," in Ceramics in Nuclear Waste Management, CONF-790420, 1979.
47. Walker, D. D., et al., "Effect of Radiation on Leaching of Bovosilicate Glass Containing Defense High Level Nuclear Waste," paper presented at the 181st National Meeting of the American Chemical Society, March, 1981.
48. Weber, W. J., "Radiation Effects in Vitreous and Devitrified Simulated Waste Glass," Proceedings, Workshop on Alternative Nuclear Waste Forms and Interactions in Geologic Media, Gatlinburg, Tennessee, 1980(a).
49. Weber, W. J., J. W. Wald, and W. J. Gray, "Radiation Effects in Crystalline High-Level Nuclear Waste Solids", paper presented at the Materials Research Society Annual Meeting, November, 1980(b).

50. Westsik, J. H., and R. P. Turcotte, "Hydrothermal Glass Reactions in Salt Brine", in G. J. McCarthy, ed., Scientific Basis for Nuclear Waste Management, Vol. 1., New York, Plenum, 1979.
51. White, W. B., "Dissolution of Crystalline Waste Forms II. The Role of Temperature in the Dissolution Process," Proceedings of ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, 1980.

FIGURES

- Figure 2.1 Five types of surfaces developed during the leaching of silicate glasses (Hench, L. L., 1977; Hench, L. L., 1975).
- Figure 2.2 Durability of low-expansion borosilicate glass vs pH of the reagent at a temperature of 95°C (Shand, E. B., 1958).
- Figure 2.3 Rate of attack on Corning 7740 in 5% NaOH at 95°C (Nordberg, M. E., n.d.).
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- Figure 2.9 Soxhlet leach rate vs change in component from centroid of PNL 11 components glass (PNL-3060; PNL-3050-2).

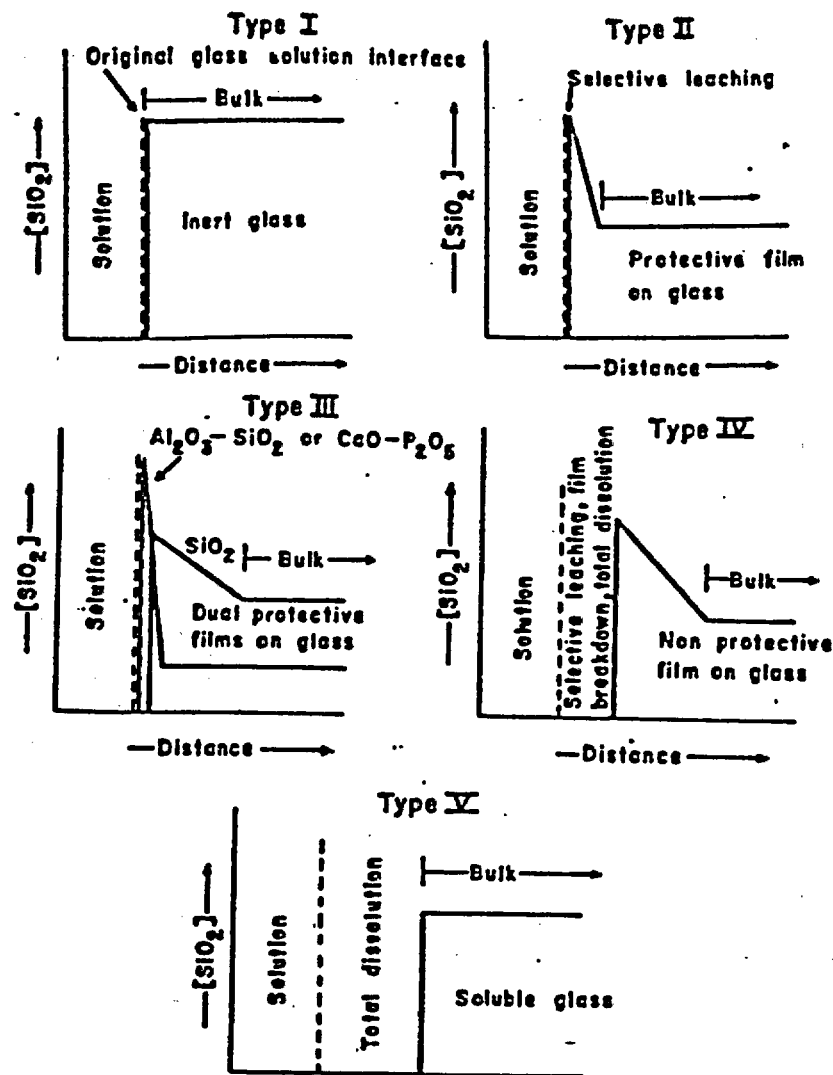


Figure 2.1 Five types of surfaces developed during the leaching of silicate glasses (Hench, L. L., 1977; Hench, L. L., 1975).

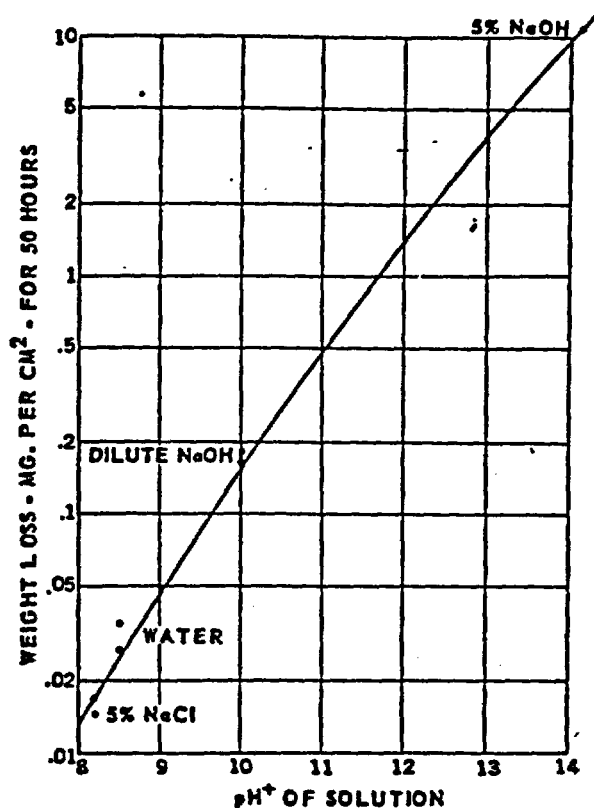


Figure 2.2 Durability of low-expansion borosilicate glass vs pH of the reagent at a temperature of 95°C (Shand, E. B., 1958).

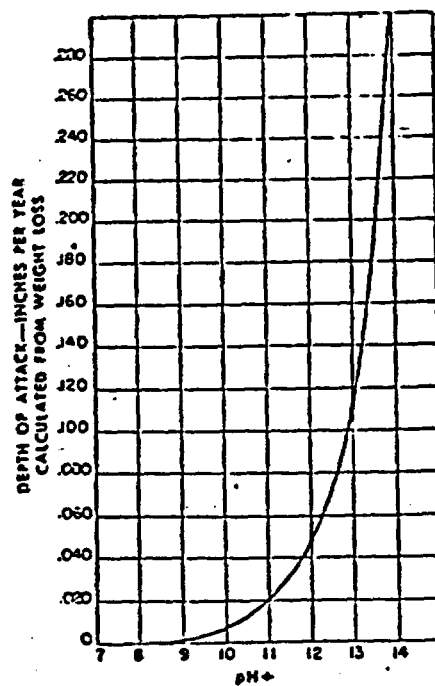


Figure 2.3 Rate of attack on Corning 7740 in 5% NaOH at 95°C (Nordberg, M. E., n.d.).

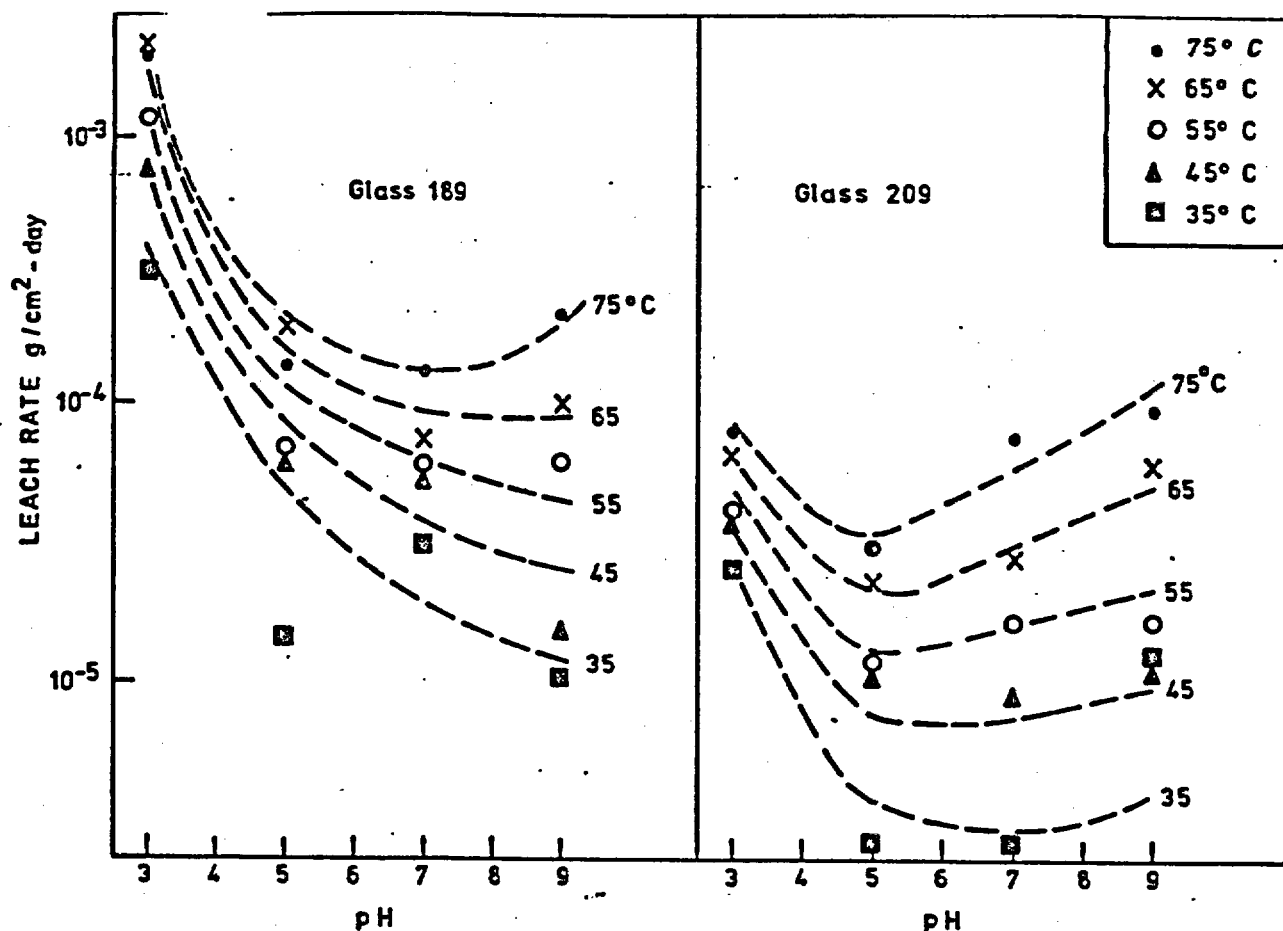


Figure 2.4 The effect of pH on the leach rate of glasses 189 and 209 at different temperatures (Boult, K. A., 1979).

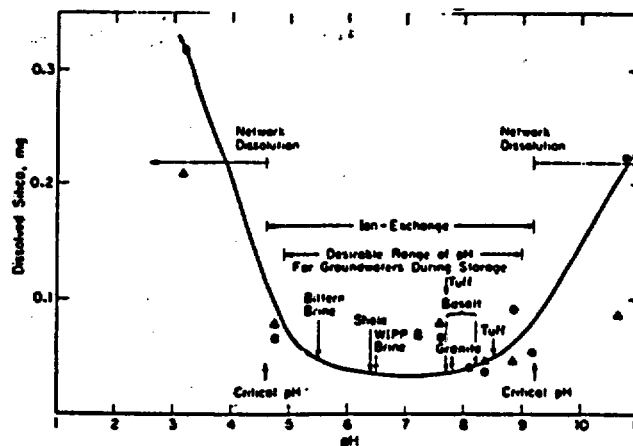


Figure 2.5 Silica dissolution vs pH curve of SRP glass (ONWI-212).

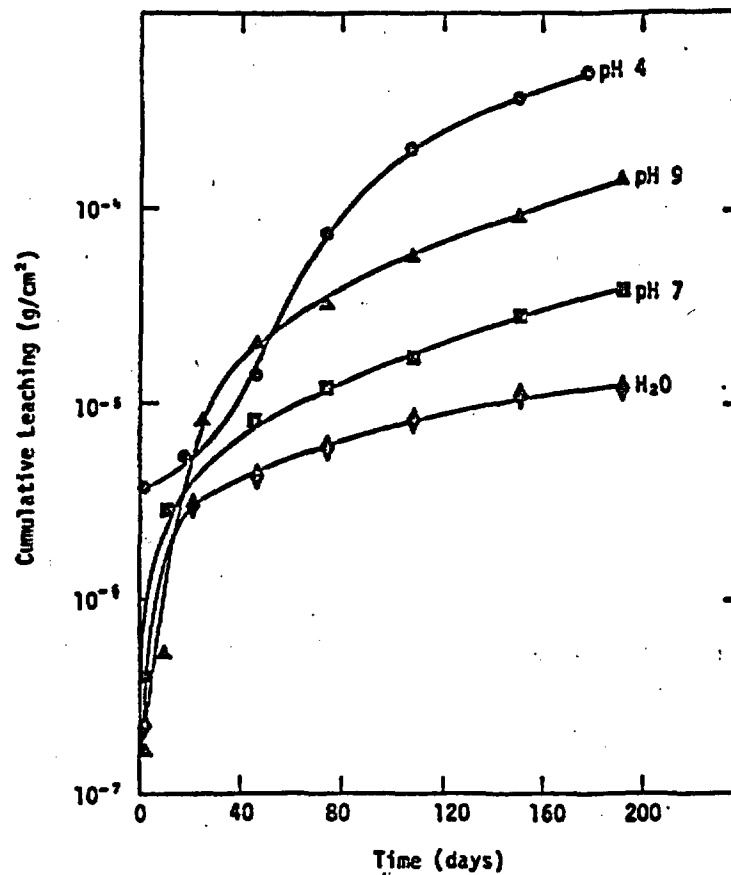


Figure 2.6 Cumulative leaching based on ^{90}Sr analysis of SRP glass (DPST-79-294).

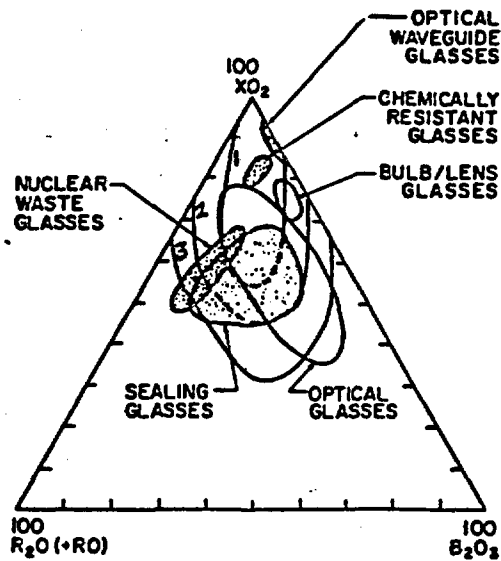


Figure 2.7 Commercial glass composition areas (Adams, P. B., 1978).

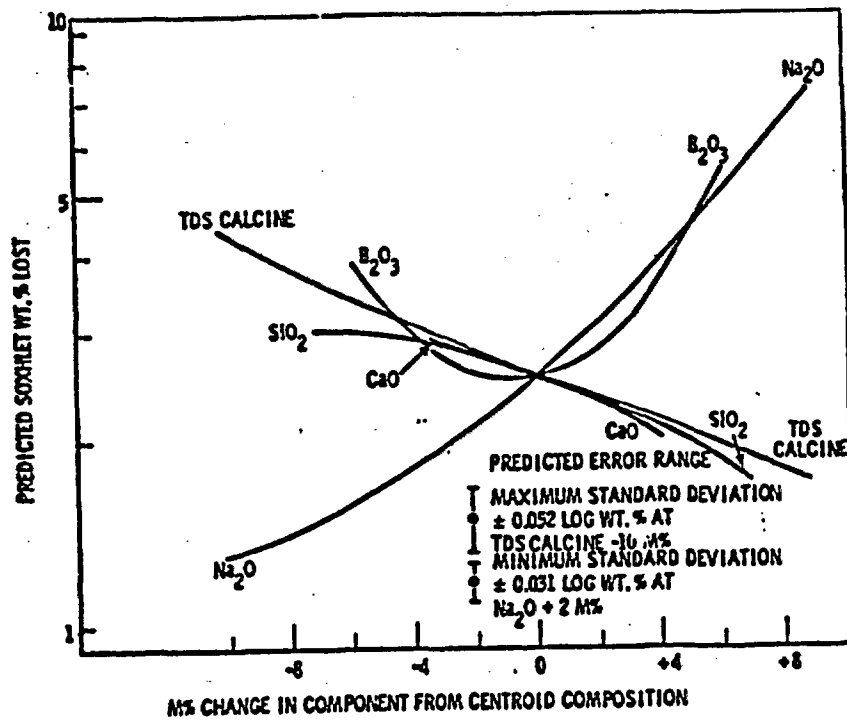


Figure 2.8 Effects of components of PNL four components glass on Soxhlet leach rate (PNL-3060; PNL-3050-2).

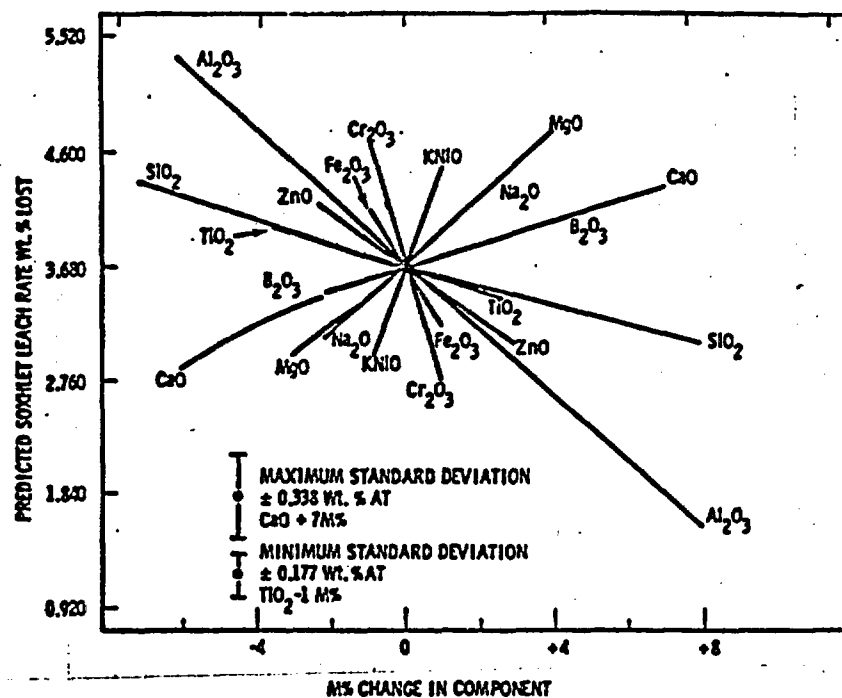


Figure 2.9 Soxhlet leach rate vs change in component from centroid of PNL 11 components glass (PNL-3060; PNL-3050-2).

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- Table 2.1 Results of Soxhlet Tests of UK Glass for Yearly Interval
 (Boult, K. A., 1979).
- Table 2.2 Summary of Defense Waste-Glass Durability (Mellinger, G. B.,
 1979).

Table 2.1

Results of Soxhlet Tests of U.K. Glass for Yearly Intervals
(Boult, K.A., 1979)

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

Table 2.2

Summary of Defense Waste Glass Durability (Mellinger, G.B., 1979)

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

APPENDIX R

TRANSPORT AND RETARDATION OF
RADIONUCLIDES IN THE WASTE PACKAGE

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1 INTRODUCTION

The waste package must be designed to contain all radionuclides during the 1000 years after emplacement. Thermal effects related to the decay of short-lived nuclides will be most severe during this period. Throughout the rest of the regulatory period, release of each radionuclide from the waste package must be less than 1 part in 10^5 per year of the maximum amount present in the waste form after the 1000 years containment period. The role of the packing material 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 design of the engineered barrier system. An understanding of the potential transport and retardation processes is necessary for predictions of the flux of contaminants from the waste package. The radionuclide release rate will depend in part upon the properties of the radionuclide species produced during degradation of the waste form and the properties of the packing material. In this appendix, the potential importance of fluid flow, Fickian diffusion, thermodiffusion, and colloid production to the transport of waste elements through the packing material will be discussed.

1.2. Government Regulatory Framework

1.2.1 Role of U.S. Agencies

1.2.1.1 DOE

The DOE is responsible for the technical research and development necessary to identify a safe repository site and for construction and operation of the site after approval by the NRC.

1.2.1.2 NRC

The NRC is responsible for reviewing and approving the DOE repository site development and issuing the appropriate construction and operating licenses consistent with regulations governing high level radioactive waste repositories.

1.2.1.3 EPA

The EPA is responsible for the protection of the environment, including protection from radioactivity releases, and for the issuance of suitable regulations and requirements.

1.2.2 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 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 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.

2 DISCUSSION

2.1 General

The general topic of radionuclide transport through the waste package can be divided into three distinct areas: (1) generation of aqueous or colloidal radionuclide species by degradation of the waste form, (2) transport of these species by fluid flow, Fickian diffusion or thermo-diffusion, and (3)

retardation of the species by processes such as sorption, chemical substitution, precipitation and ultrafiltration. The theoretical principles and experimental methods of radionuclide solubility and speciation determinations are discussed in Appendix U. Hydrothermal alteration of the waste package material is discussed in SIA Issue 2.22 and in Section 2.2.2.2 below. The degradation of the waste form is discussed in Appendix Q.

Three specific questions that are relevant to predictions of the radionuclide release rates will be addressed in this section. These are:

1. Under what conditions will diffusional (Fickian or thermodiffusion) transport dominate radionuclide migration through the backfill?
2. Under what conditions will radionuclide release be affected significantly by the production and transport of radionuclide colloids or pseudocolloids 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 of the material. The conductivity, K (cm/s) of the packing material is related to the volumetric flux, Q (cm³/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 material by the following expression

$$K = \kappa g / \mu \quad (2)$$

Where κ is the permeability (cm²), g is the gravitational acceleration and ρ and μ are the fluid density (g/cm³) and fluid dynamic viscosity (cp), respectively. The hydraulic conductivity of bentonite clay is also related to the compaction density or swelling pressure, temperature, fluid composition and hydraulic gradient. These relationships are discussed in Section 2.4.1. Values of K for potential packing materials can be found in Apps, et al., Westsik et al., Neretnieks et al., Bida and Eastwood, and Smith et al. At a compaction density of 2.1 g/cm³, Westsik measured hydraulic conductivities 5×10^{-13} cm/s, 7×10^{-12} cm/s and 1.5×10^{-12} 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 (1.2×10^4 to 7.7×10^5). These data are consistent with the values 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 first period, the bentonite is not water-saturated. During this time, water is excluded from the container but an appreciable water flow rate occurs toward the canister until 100% saturation of the packing material 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 resaturation time will depend upon the hydration rate of the dry bentonite. Based on preliminary data, PNL has estimated that several thousand years would be required for water to penetrate and saturate 20 cm of bentonite (Wheelwright, E; Bida, G.). Smith (page 2-262) gives a minimum estimate of 15-50 years for saturation of a 0.3m-thick packing assuming a pressure gradient across the barrier of 10 Mpa (hydrostatic pressure) and neglecting the effects of the swelling pressure.

During the second time period, after saturation of the packing, movement of water through the waste package will be controlled primarily by the hydraulic gradient within the repository and the hydraulic conductivity of the packing material. Assuming conservative values for these parameters, Bida et al., calculated that 1×10^5 years would be required for a volume of groundwater equal to the volume of a typical waste package to contact the container. It has been shown (Bida, G and Apps, J) that for reasonable diffusivities, diffusion dominates mass transfer through the packing material when the hydraulic conductivity is less than 10^{-11} cm/sec, for the very low hydraulic gradients (5×10^{-4} to 5×10^{-5}) expected at the BWIP site. Calculated breakthrough times for radionuclides in a clay barrier are independent of the fluid flow velocity. Thus, if the packing maintains its mechanical integrity, radionuclide transport through the packing will occur by diffusion through an effectively stagnant fluid within the interstitial pores.

2.2.2 Diffusional Transport

2.2.2.1 General principles and definitions of terms

- Chemical diffusion : a solute-mixing process in which solute species migrate from regimes of high chemical potential (thermodynamic activity) to low chemical potential. The flux and concentration of the solute can be described by Fick's laws of diffusion as described below.
- Fick's laws of diffusion: basic equations describing solute flux and concentration under flow regimes where diffusion is important. For one-dimensional diffusional transport in a fluid

$$F = -D_0 \frac{\partial c}{\partial x} \quad (\text{Fick's First Law}) \quad (3)$$

$$\frac{\partial c}{\partial t} = D_0 \frac{\partial^2 c}{\partial x^2} \quad (\text{Fick's Second Law}) \quad (4)$$

Where F and c are the solute flux and concentration, respectively, x is the direction of transport, t is time and D_0 is the molecular diffusion coefficient. Although equations 3 and 4 are written in terms of D_0 , the diffusivity in solution, the equations for diffusion in a porous media contain terms for properties of the clay such as the tortuosity, porosity, and equilibrium sorption distribution coefficients.

- Molecular diffusion coefficient (D_0): a constant, also called the diffusivity, which is characteristic of an aqueous species in a given solution (units: cm^2/s).
- Stokes-Einstein equation: an equation which relates the molecular diffusion coefficient D_0 to temperature T , viscosity of the fluid η , and the radius of the solute particles, r .

$$D_0 = \frac{kT}{6 \pi \eta r} \quad (\text{cm}^2 \text{ sec}^{-1}) \quad (5)$$

The Boltzman constant k is equal to 1.38×10^{-16} erg deg $^{-1}$; other parameters are in cgs units. The equation does not take into account any interactions between the solvent and solute that are not reflected in the viscosity of the fluid. It may be used to obtain an order of magnitude estimate of D_0 in most cases.

- Whole sediment or bulk diffusion coefficient (D_s): a diffusion constant which is characteristic of an aqueous species in a given porous media saturated by a solution of a given composition. It includes the effect of the non-linear transport path of solute molecules due to collisions with solid particles of the matrix

$$D_s = D_0 / \theta^2 \quad (6)$$

where θ is the tortuosity (Berner, R., p. 36-39).

- Dispersion Coefficient (D): a constant used in transport equations which includes the effect of dispersion, a process whereby solute molecules are diluted by both mechanical mixing during fluid advection and molecular diffusion. In general:

$$D = D_s + \alpha v \quad (6')$$

where v is the interstitial fluid velocity, D_s is the bulk diffusion coefficient and α is the dispersivity. In the low velocity fields expected in the packing material, the diffusion term will dominate the dispersion coefficient.

- Retardation factor: the ratio of the velocities of the groundwater and the contaminant. For systems in which sorption is reversible,

$$R = \frac{K_d \rho}{\phi} \quad (7)$$

where R is the retardation factor, K_d is the equilibrium sorption distribution coefficient, and ρ and ϕ are the bulk density and porosity, respectively, of the clay matrix.

Apparent diffusion coefficient (D_a): a diffusion constant for aqueous species in a porous matrix which includes the effect of retardation (units: cm^2/s). Under certain conditions this coefficient can be measured in a laboratory. When adsorption can be described by simple linear equilibrium adsorption isotherms, when changes of porosity along the flow path are negligible and when no other chemical reactions or physical processes are important, the measured apparent diffusion coefficient can be written as

$$D_a = \frac{D_0}{\theta^2 R} \quad (8)$$

where R is the retardation factor as described above.

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

$$\frac{D}{R} \frac{\partial^2 c}{\partial x^2} - \frac{v}{R} \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t} + \lambda c + \text{reaction terms} \quad (9)$$

where v is the interstitial fluid velocity, λ is the radionuclide decay constant, D is the dispersion coefficient, R is the retardation factor, c the solute concentration in the fluid, x is the direction of flow and t is time. These terms are discussed in more detail in Section 2.2.2.1. The reaction terms include expression for consumption of the radionuclide by precipitation, ultrafiltration, irreversible sorption and substitution or radionuclide production by dissolution and radioactive decay of parent nuclides.

Prediction of the ability of the packing material to contain radionuclides within the waste package will require an understanding of the values of D , R , v and the reaction terms under the conditions that prevail within the repository. Changes in the local oxidation-reduction potential, temperature, pressure, chemical and thermal stabilities of secondary phases, radionuclide solubilities and solution chemistry will affect the values of these parameters. In the following sections, progress toward obtaining relevant values of these parameters is briefly discussed.

Dispersion and Diffusion Coefficients. As discussed in Sections 2.2.1.2 and 2.2.2.1 it is anticipated that diffusion will dominate dispersion under the low fluid velocity field expected in a repository at the BWIP site. Diffusion coefficients of several radionuclides in bentonite and bentonite-quartz mixtures have been obtained at room temperature in several investigations (Smith, M; Apps, J., Torstenfelt, B., 1982a, b). Experimental methods are described in Section 2.4.2. In general, the experimental data show poor agreement with theoretical curves based on Fick's Second Law. Measured values of D_a , the

apparent diffusion coefficients, vary up to 3 orders of magnitude and increase with increasing distance from the tracer source. Molecular diffusion coefficients D_0 calculated from these data are often anomalous; they are larger than measured values for the species in pure water. The ambiguous nature of these results may be due to (1) nonlinear isotherms for the radionuclides, (2) undetected precipitation, crystallographic substitution or irreversible sorption of radionuclides by the clay and (3) non-uniform water content of the clay (Apps, J.; Torstenfelt, B., 1982a, b). Studies by Torstenfelt and others produced calculated D_0 values of 4.8×10^{-7} cm²/sec to 5.5×10^{-5} cm²/sec for the actinides. D_0 values for Cs and Sr in these studies were approximately 2×10^{-5} cm²/sec, and 3×10^{-4} cm²/sec, respectively. For comparison, D_0 values of about 10^{-5} cm²/sec can be calculated with the Stokes-Einstein equation (cf. Section 2.2.2.1) for most ionic species in water at room temperature ($\eta \sim 10^{-2}$ poise, $T = 300^\circ\text{K}$, $r = 10^{-8}$ cm) (Lerman, A.; p. 86).

As shown by the Stokes-Einstein equation, the value of the molecular diffusion coefficient is a function of temperature and fluid viscosity. The latter variable is a function of temperature, pressure and solution composition. In addition, electrical interactions between radionuclide species and other solute species will affect the value of the molecular diffusion coefficient (Berner, R., p. 34).

Equation (6') shows that the dispersion coefficient in equation (10) is dependent upon the whole sediment or bulk diffusion coefficient D , rather than the molecular diffusion coefficient. Based on a review of published data, Apps (1982) suggested that a range of D values of 1×10^{-6} cm²/sec to 5×10^{-6} cm²/sec was reasonable for modeling generic radionuclide transport in the packing material. Equation (6) indicates that the value of D depends on the molecular diffusion coefficient and the tortuosity of the sediment. Thus, the values of the dispersion coefficients of radionuclides in the packing material depend on a large number of environmental parameters and material properties. At present, existing data are insufficient to predict the values of these coefficients under the environmental conditions that will prevail in the packing material at different times during the repository post-closure period. Experimental investigations to determine the dispersion coefficients under conditions relevant packing material performance are necessary.

Retardation Factors

The retardation factor due to reversible sorption for solute transport in porous media was defined by equation (7) in Section 2.2.2.1.

$$R = 1 + K_d \rho / \phi \quad (7)$$

A discussion of restrictions upon the use of equation (7) and methods for determining radionuclide distribution coefficient (R_d 's or K_d 's) for geologic media may be found in Appendix T.*

*We use the symbol R_d to signify an experimentally-determined radionuclide distribution coefficient where we do not assume that equilibrium has been achieved. Although they are called "sorption ratios," there is no assurance that sorption is the only chemical process occurring during the experiments. We use the term K_d in its classical sense, i.e., ideal ion exchange equilibrium involving trace constituents.

For reversible linear sorption, the retardation factor and radionuclide distribution coefficient will be independent of concentration. For several elements, however, nonlinear isotherms such as the Langmuir or Dubinin-Radushkevich isotherm must be used to calculate concentration-dependent retardation factors. In general,

$$S = f(c) \text{ (isotherm equation)} \quad (10)$$

$$R = 1 + [\rho/\phi]f'(c) \quad (11)$$

where $f'(c)$ is the first derivative of the sorption isotherm with respect to concentration, S is equilibrium concentration of the sorbed ion per gram of solid and c is the equilibrium concentration of sorbing ion in the bulk solution.

The chemical reactions described in Appendix T for radionuclide migration in geologic environments will also be important for interactions between groundwater radionuclides and the packing material within the waste package. These processes include: ion exchange, chemisorption, hydrolysis precipitation, coprecipitation, and precipitation and changes in speciation due to redox reactions. Changes in the temperature of the radionuclide-groundwater-packing material system will introduce other chemical reactions. Basalt will react with the ground-water to form secondary minerals such as smectites and zeolites and the composition of the solution will change. Experimental results from high temperature reactions of basalt with sea water and groundwater from the Columbia River Basalts suggest that concentrations of F^- , K^+ , SiO_2 , Fe^{2+} , Mn^{2+} , CO_3^{2-} , HCO_3^- will increase and that the pH and sodium content of the solution will decrease. Analyses of synthetic groundwater solutions contacted with secondary minerals (98% smectite) from the Hanford Site indicate a significant increase in Mg^{2+} , Ca^{2+} , SO_4^{2-} and SiO_2 concentrations. These changes in the solution composition and the mineralogy of the substrate can affect the R_d values.

Determinations of R_d 's for selenium, strontium, technetium, iodine, cesium, radium, neptunium, americium, plutonium and uranium have been carried out at 23°C, 60°C, 150°C and 300°C with crushed basalt under oxidizing conditions (Ames, 1980a; 1980b; Salter, P.). 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 were poorly sorbed by crushed basalt. Cationic species (Sr^{2+} , Cs^+) or easily hydrolyzable (Am, Pu) species were more strongly sorbed. Sorption ratios of Np, I and Tc did not show a dependence on temperature under these conditions. The temperature effects for the other elements and possible explanations for the results are described in Table R-1. The experimental methods are discussed in Section 2.4.3.

In general, the high-temperature R_d values presented in DOE/RL 82-3 and RHO-BWI-LD-48 (Salter, P.) cannot be treated as true K_d values. Reversible ion exchange of simple ions or complexes generally is an exothermic reaction; values of K_d should therefore decrease with increased temperature (Salter, P.). The increases of R_d values at elevated temperatures as described in Table T-1 suggest that other chemical reactions are dominating the

experimental results. These processes may include (1) precipitation of the trace elements of interest as sulfates, carbonates or sulfides, (2) incorporation of the trace elements into the crystal structures of secondary hydrothermal-minerals, (3) destabilization of non-sorbing neutral or anionic complexes in favor of strongly-sorbing cationic complexes or charged colloids (cf. Langmuir, D. for discussion for this effect in uranium speciation), (4) sorption of trace elements onto hydrothermal secondary minerals.

Rd values for several other candidate packing materials have been obtained at 23°C and 60°C under oxidizing conditions (Salter, P., 1982b; Westsik, J; Smith, M. J.). Commercially-available samples of bentonite and zeolite or samples of smectite from fractures in Columbia River Basalts were used for determinations of the Rd's for Sr, Cs, Am, Np, Pu, U, I, Tc, Se, and Ra in synthetic basalt ground water. At 23°C, americium, cesium and plutonium generally exhibited high (>1,000 ml/gm) Rd values; strontium exhibited high to moderate (>100 ml/gm) Rd values; neptunium, radium and uranium exhibited moderate to weak (>10 ml/gm) Rd values and iodine, technetium, and selenium were poorly sorbed (Rd = 0-10 ml/gm). No significant effect of temperature on the Rd values was observed for Se, Tc, I, Np, Am, Pu, and Ra over the range 23°C - 60°C. Sorption ratios for Sr and U increased over the same temperature range. The Rd values for Cs on secondary minerals from the basalts decreased over the temperature range 23°C to 150°C and increased slightly from 150°C to 300°C (Ames, 1980b).

Reducing alkaline conditions will be re-established within the repository after closure of the facility. The length of time required for this process is not known at present. It is possible that reducing conditions will prevail during the thermal period of the repository lifetime. High-temperature sorption data for basalt-bentonite-water systems under reducing conditions, however, are not available. Results from basalt sorption experiments at 23°C with a hydrazine reducing agent suggest that Rd values for uranium, technetium, plutonium are higher under reducing conditions than under oxidizing conditions (Salter, P.; Barney, G., Smith, M.). Available Rd data from these experiments should not be used as K_d values; reduction and precipitation of aqueous species as reduced solid phases has probably dominated the experimental results. The effects of temperature upon the speciation of the radionuclides under reducing condition is not understood. Extrapolation of results obtained at low temperatures to obtain Rd values at elevated temperatures is difficult to do at this time.

Radionuclide Retention times

In a diffusion experiment, the retention time is defined as the time required for breakthrough to occur across a barrier. For a barrier thickness of Z meters, the retention time for a diffusion process would be given by

$$t = 0.1z^2/D_a \quad (12)$$

(Torstenfelt, B., 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. Retention times calculated from diffusion coefficients for long-lived radionuclides in spent fuel suggest that isotopes of Sr, Cs, Th, Pu, Ra, might be retained in a 1-meter-thick compacted

bentonite or bentonite-quartz mixture until they decay to relatively low (< 5%) fractions of their original inventories (Smith M. J.; Neretnieks, I., Torstenfelt, B., 1982b). Thicker barriers would be required for retention of neptunium.

2.2.3 Thermodiffusion (Soret Effect)

2.2.3.1 General Principles

Diffusion of chemical species along a thermal gradient is known as the Ludwig-Soret or Soret effect. The flux of solute induced by the temperature gradient is added to that driven by the chemical potential (concentration) gradient. For transport in a fluid, the solute flux, J , in one dimension can be written as:

$$J = D_0 \frac{\partial c}{\partial x} - D_T c \frac{\partial T}{\partial x} \quad (14)$$

The first term is the diffusive flux due to Fickian diffusion; the second term is the thermodiffusive flux. D_T is the coefficient of thermal diffusion, T is the temperature and c is concentration of the solute. Equation (14) can also be written as

$$J = -D_0 \left(\frac{\partial c}{\partial x} + s c \frac{\partial T}{\partial x} \right) \quad (15)$$

where the Soret coefficient s is equal to D_T/D_0 (deg^{-1}). For common electrolytes and constituents of natural waters, values of the Soret coefficient are in the range of 10^{-3} to 10^{-2} deg^{-1} (Lerman, A., p. 98-99).

During the thermal period of the repository lifetime a thermal gradient will be established across the width of the packing material. The maximum gradient will occur approximately 5 years after emplacement ($\Delta T \approx 120^\circ\text{C}$ for CHLW in an unsaturated packing) DOE/RL 82-3, Fig. 11-4). At this time, however, appreciable diffusion and radionuclide release may be precluded by the absence of interstitial water in the packing material. Available estimates of the time required to resaturate the packing with water range from 15 years to several thousand years (cf. Section 2.2.1.2). It is expected that after one thousand years there will be no temperature drop across the barrier (DOE/RL 82-3, Fig. 11-4). The possible temperature differences that may occur across the resaturated packing material during the lifetime of the repository depend upon the rehydration rate of the packing material under the influence of the changing thermal field as discussed in Sections 2.2.1.2 and 2.4.1.2.

The relative importance of the thermodiffusive flux compared to the chemical diffusive flux can be estimated from rearrangement of equation (15).

$$\frac{J_D}{J_T} = \frac{1}{s c} \cdot \frac{\partial c}{\partial x} \cdot 1/\frac{\partial T}{\partial x} \approx \frac{\Delta c}{c} \cdot \frac{1}{s \Delta T} \quad (16)$$

Where J_D and J_T are the fluxes due to chemical diffusion and thermal diffusion, respectively; Δc and ΔT are the solute concentration difference and temperature difference across the barrier; c is the average concentration of the species within the barrier. The remaining terms have been described above. It can be seen that the Soret effect will become important compared to Fickian

diffusion when the concentration gradient is small, the average concentration is high, and/or the thermal gradient is high. The concentration gradient and average concentration of each radionuclide will depend upon its solubility limit, its initial concentration in the waste form, and its leach rate. The value of $\Delta c/c$ will vary with both time and temperature. The relative importance of thermodiffusion must be evaluated from equation (16) on an element-specific basis for various times during the repository history.

2.2.4 Production and Migration of Radiocolloids and Pseudo-colloids

2.2.4.1 General Principles and Definitions

A nontrivial fraction of radionuclides released from the waste form could be present as pseudocolloids or true colloids. Chemically, colloids could behave differently than dissolved species; different transport and retardation mechanisms may be important in determining their migration behavior. Colloids refer to systems of large macromolecules or particles ($1 \text{ nm} < r < 10^3 \text{ nm}$) dispersed in an aqueous phase. The colloids found in most geologic systems are metastable (lyophobic) colloids which will aggregate to form non-colloidal solids within time periods of hours to years (Apps, J.). Colloids may form either by condensation or by dispersion. Condensation colloids form when the aqueous solution becomes supersaturated with respect to the formation of an insoluble solid phase. Often, a kinetically-favored, thermodynamically metastable phase will precipitate in a colloidal suspension. Rapid, sharp changes in Eh, pH or groundwater composition can cause such supersaturation. Dispersion colloids form through degradation of bulk matter into colloidal-size particles. The importance of this process is well demonstrated for clays and gel layers forming on borosilicate glass (Apps, J.) and is discussed in Appendix Q.

Flocculation is the aggregation of colloids into larger particles followed by sedimentation by gravitational forces. The stability of a colloid system to flocculation depends upon the flow rate of the aqueous phase and the size and surface charge of the particles. The surface charge depends on both the charge arising from ionic substitutions within the colloid and the chemistry of the aqueous solution. Counter ions, which may be absorbed onto the colloid surface from solution, will decrease the repulsive force between the charge particles and allow the particles to flocculate. The size, stability and other properties of colloids are dependent upon their mode for formation, chemical constituents and the flow rate and chemistry of the solution. In natural systems, the nature of the colloidal particles that occur can change with time, temperature and physico-chemical conditions.

Pseudocolloids of radionuclides form when dissolved species of the radio-elements sorb onto the charged surfaces of pre-existing colloidal-sized particles. Such particles could be formed by degradation of clay minerals or borosilicate glass or the precipitation of insoluble phases of other groundwater constituents (e.g., $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$).

2.2.4.2 Applications to Waste Package Performance

The potential for production of colloids of the actinides and other metals present in the waste form exists. Oxides, hydroxides, phosphates, carbonates

and silicates of these elements are very insoluble. Supersaturation of the solution contacting the waste form could occur under stagnant fluid conditions. The formation of true colloids of Am, Pu, Np has been observed in saturated solutions and in solutions in contact with borosilicate glass (Avogadro, A; Olofsson, U.). The occurrence of colloidal-size Pu(IV) polymers is discussed by Apps, J. et al.

Pseudocolloids with clay, silica or ferric hydroxide particles could form with all of the radionuclides under certain conditions. Aluminosilicate and silica colloids exhibit a negative surface charge over the pH range expected under natural conditions. Such particles will attract cationic complexes of many of the radionuclides (e.g., Cs^+ , UO_2^{2+} , UO_2OH^+ , Sr^{2+} , Ra^{2+} , $\text{Am}(\text{OH})_2^+$, AmOH^{2+}). Oxides and hydroxides of metal components in the canister and waste form exhibit a range of points of zero charge (ZPC). Some particles with positive surface charges might form under the range of pH conditions expected during the lifetime of the repository (cf. Appendix S). The formation of a leached silica gel layer on the surface of the glass has commonly been observed in leach studies (cf. Appendix Q and cited references). Disintegration of this unstable layer into colloidal-size silica particles is possible. Leaching of borosilicate glass in the presence of iron results in the formation of iron silica colloids which may scavenge soluble radionuclide species from solution. This process produces radionuclide pseudocolloids and leads to an increase of the release rate of the radionuclides from the waste glass (McVay, G. L.).

The production of radionuclide colloids and pseudocolloids will be important to radionuclide release from the waste package only under certain hydraulic conditions. In stagnant systems, colloids may form but particulate transport will be limited to diffusion by Brownian motion of microcolloids. In porous media with nontrivial fluid flow, colloids can be retained by packing material by ultrafiltration. This behavior has been observed in clay soil columns (Avogadro, A). In such systems, the release rate of the radionuclides would be determined by dissolution of the colloids and transport by soluble species. Apps, J. et al. used a continuum model to compare diffusive fluxes and gravitational settling rates of colloids of different particle sizes in a viscous fluid. Based on the results of these calculations they suggested that gravitational settling will efficiently remove colloidal particles of all size fractions from diffusional transport in porous or fractured media having pore or fracture apertures smaller than approximately 1 mm. Processes such as physical adsorption, chemisorption and pore closing would enhance the rates of removal.

Convective transport through larger fractures was not considered in the above calculations. The transport of radionuclide colloids or pseudocolloids might be more important in accident scenarios wherein the packing material is breached and large fluxes of water contact a previously-formed gel surface layer on the waste glass (Avogadro, A).

3.0 Information Needs

Currently available data suggest that under normal conditions (i.e., non-accident scenarios) appreciable solute transport in the packing material will not occur during the first thousand years following emplacement of the waste package. After resaturation of the packing material with water, radionuclide

transport will occur dominantly by diffusion through interstitial fluid. The available data and calculations suggest that choice of the proper packing materials and chemical additives can buffer the water within the engineered barrier and assure sufficiently long retention times for most radionuclides. Much of the data used to reach these conclusions, however, were collected under conditions that are not representative of expected repository conditions. Extrapolations to repository conditions are often made without a firm theoretical understanding of the chemical processes responsible for the effects observed in the laboratory. Equation (9) in Section 2.2.2.2 shows that values of the dispersion and diffusion coefficients D and D_s , the retardation factor R and the interstitial velocity v are important to predictions of radionuclide transport in the packing material. It is important to obtain accurate values of these parameters under realistic conditions. The radionuclide distribution coefficient K_d , the hydraulic conductivity K and the molecular diffusion coefficient D_0 are used to calculate values of these parameters. In Section 2.4, the methods used to obtain values of these constants are described. In addition, previous investigations of the Soret effect are discussed. Methods used to identify radionuclide colloids are described in Appendix U.

2.4 Methods

2.4.1 Hydraulic Conductivity

2.4.1.1 Methods of Measurement

Test methods to determine the hydraulic conductivity of bentonite clays as functions of swelling pressure, compaction density and hydraulic head are described in Westsik, J.; Bida G. and Pusch, R. In experiments performed at PNL (Westsik, J.), the permeating fluid was pumped under high pressure into a permeability cell which contained a column of compacted, powered packing material. The fluid was collected in a preweighed vessel after it has flowed through the column. The volumetric flow rate was determined by weighing the effluent as a function of time. The hydraulic conductivity K and intrinsic permeability k were determined from equations (1) and (2) respectively.

2.4.1.2 Uncertainties in Available Data

The hydraulic conductivity of the packing is dependent upon compaction density, temperature and hydraulic gradient. The compaction density in turn is 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 nearly zero because of the high temperatures within the waste package. Water will only be present as vapor in the outer layers of the waste packing. The compaction density will change as the waste package cools and the packing rehydrates. Further BWIP investigations of the performance of the packing material should examine the compaction density of packing material as a function of the degree of rehydration as the water vapor in the clay returns to the liquid state (Bida, G.).

The dependence of hydraulic conductivity on hydraulic gradient is discussed in Westsik, 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 the high-gradient experiments at PNL may lead, therefore, to overestimates of fluid flow within the BWIP waste package.

The dependence of hydraulic conductivity on temperature can be related in part to the temperature dependencies of the compaction 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, G. The effect of the variation of other environmental parameters such as groundwater composition, redox potential and radiation field strength should also be considered in future studies of fluid flow through packing material.

2.4.1.3 Thermomechanical Effects on the Packing Material

The packing material around the waste canisters in a repository is expected to experience a constantly changing thermal/mechanical/hydrological environment, especially during the first several hundred years following emplacement of waste.

The primary function of the packing (previously termed discrete backfill) is to minimize radionuclide transport by groundwater flow control and geochemical retardation. The hydraulic conductivity, which relates the flow rate to the hydraulic gradient, of the candidate packing material(s) (e.g., benetomite/basalt mixture) is subject to alterations due to the changing repository environment. The initial hydraulic conductivity depends on the compaction density and the moisture content. Many other parameters will affect the subsequent hydraulic conductivity of the packing following emplacement. The temperature, swelling pressure, thermomechanical stresses, hydrothermal stability, structural integrity, hydration/dehydration directly affect the hydraulic conductivity. These additional parameters or processes are, in general, interdependent, which makes it difficult to quantify the influence of any one parameter on the hydraulic conductivity. Moreover, each of the parameters identified has uncertainties in the predicted response. For instance, the transient thermal response at the waste package depends strongly on the thermal conductivity of the packing, which in turn, depends on the composition, degree of compaction, temperature, and moisture content (Altenhofen, M. K.) throughout the time range of interest. It is noted that the temperature can be predicted reasonably accurately provided the thermal and physical material property data are free of uncertainty.

The swelling pressure will affect the porosity and, hence, the hydraulic conductivity of the packing. But the swelling pressure itself is a function of temperature, hydraulic pressure and the thermomechanical stresses. According to Bida and Eastwood, a higher compaction density implies a higher swelling pressure. On the other hand, a more compacted packing represents a higher resistance to mechanical deformation, thus making it progressively more difficult to collapse the remaining pores.

The process of excavation and building tunnels will alter the in-situ stresses in the near-field. Even before the waste is emplaced, stress concentrations will exist in the vicinity of the tunnels. The stress field will alter further after the heat generating waste canisters are emplaced.

It is important to consider the thermomechanical stresses acting at the waste package boundary and not just the pre-excavation in-situ stresses. Again, if the thermal conductivity of the packing is low, higher canister surface temperatures and higher temperature gradients across the packing may be expected. The mechanical properties (Young's modulus, shear modulus) will dictate the stress state in the packing. These properties, in general, will also depend on temperature for a given density and moisture content.

At the time of emplacement, the packing will be at ambient temperature, but will experience elevated temperatures within a few years. For a conceptual spent fuel repository in basalt, calculations (Altenhofen, M. K.) show that peak temperatures in the waste package will range between 190°C with the peak occurring within the first decade of emplacement. Since the packing is likely to have an initial moisture content, but not saturated, a cycle of drying and wetting is very conceivable. If unsaturated conditions occur in the surrounding rock, it is even likely that multiple drying/wetting cycles might take place. Such drying could cause cracks or fissures in the packing that can substantially enhance the permeability (and hydraulic conductivity). Most engineering materials tend to become more ductile (i.e., less brittle) with increasing temperature. However, the potential drying in the packing associated with increasing temperature is expected to have the opposite effect; i.e., it would tend to make it more brittle. Whether the net effect would be favorable or not can only be confirmed by conducting tests in realistic environments. If cracks and fissures do form due to the dry/wet cycling process, they could alter the flow and transport significantly. Fracture flow (advection) could become dominant through the packing with an associated increase in flow rates and greater chance of colloid transport.

It is unlikely that tensile stresses would be experienced by the packing. But failure in compression could occur that would jeopardize the structural integrity of the packing. Therefore, the compressive strength as a function of temperature should be a design parameter.

2.4.2 Diffusion Coefficients

2.4.2.1 Methods of Measurement

Apparent diffusion coefficients are given by Fick's Second Law of Diffusion for one dimensional diffusion.

$$\frac{dc}{dt} = \frac{d}{dx} \left(D_a \frac{dc}{dx} \right) \quad (17)$$

Laboratory determinations of apparent diffusion coefficients often use a planar source of the radionuclide of interest which diffuses into a clay cylinder of effectively infinite length (Torstenfelt, 1982a, b). The solution of equation for this system is (Crank, J.):

$$\frac{c}{M} = \frac{1}{2 (\pi D_a t)^{1/2}} \exp (-x^2/4D_a t) \quad (18)$$

where c is concentration (mol/cm^3), M is the total amount of diffusing species added (mol/cm^2), x is the distance from the source (cm), D_a is the concentration independent apparent diffusivity (cm^2/s) and t is the time (s). In these experiments, the clay cylinder is placed in a synthetic groundwater which has been pre-equilibrated with the clay. After a "sufficient" contact time (often 2-3 months) the clay cylinder is cut open and the concentration of the tracer at several distances from the source is determined. The molecular diffusion coefficient, can be obtained from the apparent diffusion coefficient through solution of equations (7) and (8).

2.4.2.2 Uncertainties in Available Data

As discussed in Section 2.2.2.2, the data produced in many of these experiments cannot be fitted to equation (18). Equations (7) and (8) are valid only when simple linear reversible isotherms describe the sorption behavior, when changes of porosity and water content along the flow path are negligible, and when other chemical reactions such as precipitation are not important. In general, data are not sufficient to determine if these assumptions obtain in the experiments. In addition, extrapolation of the results obtained at room temperature and pressure should not be extrapolated to repository conditions without justification based on kinetic and thermodynamic arguments. Ideally, diffusion coefficients should be measured under the temperatures, pressures and chemical conditions expected at the repository. Hydrothermal interactions between waste package components, radionuclides, and other solutes however, may make these determinations very difficult.

2.4.3 Radionuclide Distribution Coefficients

2.4.3.1 Methods of Measurement

Techniques for high-temperature batch R_d determinations are described by Ames, (1980a, 1980b) and Salter P., (1982a, 1982b). In these studies, radionuclide-basalt reactions are investigated at elevated temperatures ($150\text{--}300^\circ\text{C}$) and pressures ($6.9\text{--}27.6$ Mpa) in Inconel pressure vessels. Precautions are taken to minimize sorption of the radionuclide on the walls of the pressure vessel and sample ports. Analyses of both solution and solid phases are carried out after the R_d determinations to determine changes due to the high temperature reactions.

Static and dynamic methods for determination of R_d values at lower temperatures are discussed in Appendix T. Although the available high-temperature R_d data have been obtained by the batch (static) technique, dynamic (flow-through) systems could be used in future experiments. The general comments presented in Appendix T concerning experimental methods, presentation of data, and the uncertainties associated with the extrapolation of R_d values obtained in the laboratory to modeling radionuclide transport under natural conditions apply to sorption and retardation at both high and low temperatures.

2.4.3.2 Uncertainties in Available Data

As discussed in Section 2.2.2.2 and Appendix T, R_d values are empirical values which may include the effects of several chemical processes such as precipitation or substitution in addition to ion exchange. They cannot be equated with

K_d values (cf. footnote, p. 9); calculations of retardation factors with R_d values in place of K_d values in equation (7) may lead to underestimates of radionuclide discharge. Elimination of the effects of other chemical reactions through improved experimental technique and the use of isotherm equations in place of single value R_d 's may allow more accurate calculations of retardation factors (cf. equation (11)). Such techniques may include the introduction of the tracer in pre-equilibrated ground water as the aqueous species produced by dissolution of the waste form. (Nowak, 1982.) A multi-stage pre-equilibration procedure might include the following steps: 1) pre-equilibration of ground water with packing material at elevated temperature and pressure and low Eh to produce a reaction solution and 2) leaching of the waste form with the reaction solution at elevated temperature and pressure and low Eh to produce the tracer and blank solutions. The tracer solution produced in step 2 above could then be contacted with the solid substrate for the R_d determination. Such a procedure could eliminate some of the processes which have obscured the effects of sorption in previous R_d measurements. In this way, the effects of sorption could be included in the retardation factor R while other chemical processes could be included separately in the reaction terms in equation 9.

2.4.4 Soret Diffusion Coefficients

2.4.4.1 Methods of Measurement

Thermodiffusion in binary aqueous systems has been studied extensively (for compilations of values at Soret coefficients of common electrolytes see Lerman, A.). Soret coefficients for species in fluid phases are obtained by the use of reaction cells filled with solutions of uniform composition with two end plates maintained at different temperatures. At steady state, i.e., net diffusive flux equals zero, the Soret coefficients can be obtained by rearrangement of equation (15)

$$J = 0 = -D_0 \frac{\partial c}{\partial x} + s c \frac{\partial T}{\partial x} \quad (19)$$

$$- \frac{1}{c} \frac{\partial c / \partial x}{\partial T / \partial x} = s \quad (19')$$

The Soret coefficient is obtained by evaluation of the concentration gradient in the presence of a uniform temperature gradient.

Measurements of Soret coefficients are described in Thornton, 1982, 1983 and Seyfried, 1982a, 1982b. In these experiments, temperature and solute concentrations were measured along a sediment core across which a temperature difference of 200°C was maintained. The slope of experimental curves on semi-log plots ($\ln c$ vs. T) is equal to the Soret coefficient. This can be seen by rearrangement of equation (19) and integration over the limits of concentration and temperature

$$\Delta \ln c = -s \Delta T \quad (20)$$

2.4.4.2 Uncertainties in Available Data

At present there are few available values for Soret coefficients of the radionuclides relevant to waste management. There are abundant data for simple salts of sodium, potassium, magnesium and strontium at low (25°C-40°C) temperatures in water (Lerman A., p. 98-99). Soret coefficients for Cl, Na, Ca, and Mg were obtained at higher temperatures (100°C-300°C) in cores of inert alumina particles and silty clay which were saturated with artificial sea water (Thornton, E). Although experiments with inert alumina were designed to minimize high temperature alteration of the substrate by the fluid phase, precipitation of carbonates and hydroxides may have occurred. Considerable reaction between the pore fluid and sediment occurred in experiments using a clay matrix. In view of the paucity of data concerning radionuclide solubilities and potential substitutions into secondary minerals, it is anticipated that the determination of Soret coefficients for radionuclides in potential packing materials would be a complicated experimental study.

REFERENCES

1. Altenhofen, M. K., Waste Package Heat-Transfer Analysis: Model Development and Temperature Estimates for Waste Packages in a Repository Located in Basalt, RHO-BWI-ST-18, Richland, WA, October, 1981.
2. Ames, L. L. and McGarrah, J. E., 1981a, High-Temperature Determination of Radionuclide Distribution Coefficients for Columbia River Basalts, RHO-BWI-C-111/PNL-3250, Rockwell Hanford Operations/Pacific Northwest Laboratory, Richland, Washington.
3. Ames, L. L. and McGarrah, J. E., 1981b, Basalt-Radionuclide Distribution Coefficient Determinations, FY 1980 Annual Report, PNL-3146, Pacific Northwest Laboratory, Richland, Washington.
4. Apps, J. A. and others, Status of Geochemical Problems Relating to the Burial of High-Level 1981, prepared for NRC by Lawrence Berkeley Laboratory, August 1982.
5. Avogadro, A., and others, Underground Migration of Long-Lived Radionuclides Leached From a Borosilicate Glass Matrix, IAE-SM-257/73, International Symposium on Migration in the Terrestrial Environment of Long-Lived Radionuclides from the Nuclear Fuel Cycle; July 1981.
6. Barney, G. S., Radionuclide Reactions with Groundwater and Basalts from Columbia River Basalt Formations, RHO-SA-217, Rockwell Hanford Operations, Richland, Washington, 1981.
7. Berner, R., Early Diagenesis: A Theoretical Approach, Princeton, New Jersey, 1980, 241 p.
8. Bida, G. and Eastwood, D., Discrete Backfill Testing Required to Demonstrate Compliance with 1000-Year Radionuclide Containment, NUREG/CR-2755, Brookhaven National Laboratory, May 1982.
9. Champ, D. R., Merritt, W. F., and Young, J. L., Potential for the Rapid Transport of Plutonium in Groundwater as Demonstrated by Core Column Studies, in The Scientific Basis for Radioactive Waste Management, Vol. 5, W. Lutze, Ed. (North-Holland, New York, 1982), pp. 329-336.
10. Crank, J., The Mathematics of Diffusion, (Oxford University Press, London, 1956), 347 p.
11. DOE/RL 82-3. Site Characterization Report for the Basalt Waste Isolation project, November 1982.
12. Freeze, R. and Cherry, J., Groundwater, (Prentice-Hall, New Jersey, 1979), 604 p.
13. Langmuir, D., Uranium-Solution Mineral Equilibrium at Low Temperatures with Application to Sedimentary Ore Deposits, Geochim. Cosmochim. Acta. 42: 547-567, 1978.

14. Lerman, A., Geochemical Processes (Wiley, New York, 1979), 481 p.
15. McVay, G. L., and C. Q., Buckwalter, The Effect of Iron on Waste Glass Leaching, PNL-SA-10474, Pacific Northwest Laboratory, Richland, Washington, Washington, May 1982.
16. 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, IAEA, 1980) IAEA-SM-243/108, pp.
17. Nowak, J., 1982.
18. Olofsson, U., Allard, B., Anderson, K., and Torstenfelt, B. Formation and Properties of Americium Colloids in Aqueous Systems, in The Scientific Basis for Nuclear Waste Management, Vol. 4, S. Topp, Ed. (North-Holland, New York, 1982), pp. 191-199.
19. Pusch, R., Water Percolation Effects on Clay-Poor Benetionite/Quartz Buffer Material at High Hydraulic Gradients, KBS Technical Report 79-17, 1979.
20. Rickert, P. G., Americium Migration in Basalt and Implications to Repository Risk Analysis, CONF-8010130-8, Argonne National Laboratory, Illinois, 1980.
21. Salter, P. F., Ames, L. L. and McGarrah, J. E., Sorption of Selected Radionuclides on Columbia River Basalts, Informal Report, RHO-BWI-LD-48, August 1981.
22. Salter, P. F., Ames, L. L. and McGarrah, J. E., Sorption of Selected Radionuclides on Secondary Minerals Associated with Columbia River Basalts, RHO-BWI-LD-43, Rockwell Hanford Operations, Richland, Washington, 1981.
23. Seyfried, W. E. and Thornton, E. C., Experiment and Theoretical Modeling of Hydrothermal Processes in the Near-field Environment: Subseabed Disposal Annual Report, Sandia National Laboratories, Albuquerque, New Mexico, January to October 1982.
24. Smith, M. J., and others, Engineered Barrier Development for a Nuclear Waste Repository Located in Basalt, RHO-BWI-ST-7, Rockwell Hanford Operations, May 1980, pp. 258-272.
25. Thornton, E. C., Seyfried, W. C. and Brush, L. H., Waste Glass - Seabed Sediment Interaction: Observations of the Soret Effect, in Workshop on the Leaching Mechanisms of Nuclear Waste Forms, May 19-21, 1982, pp. 227-238.
26. Thornton, E. C., and Seyfried, W. E., Jr., The Soret Effect: Potential for Thermodiffusional Transport in a Nuclear Waste Repository, Geol. Soc. America Abstracts with Programs, V. 14, 1982, p. 631-632.

27. Torstenfelt, B. and others, Diffusion Measurements in Compacted Bentonite, in The Scientific Basis for Nuclear Waste Management, Vol. 4, S. V. Topp, Ed. (North-Holland, New York, 1982), pp. 295-302.
28. Torstenfelt, B. and others, Transport of Actinides Through a Benetonite Backfill, in The Scientific Basis for Nuclear Waste Management, Vol. 5, W. Lutze, Ed. (North-Holland, New York, 1982), pp. 329-336.
29. Westsik, J. H., and others, Permeability, Swelling and Radionuclide Retardation Properties of Candidate Backfill Materials, in The Scientific Basis for Nuclear Waste Management, Vol. 4, S. V. Topp, Ed. (North-Holland, New York, 1982), pp. 329-336.
30. Wheelwright, E. J., and others, Development of Backfill Materials as an Engineered Barrier in the Waste Package System--Interim Topical Report, PNL-3873, Pacific Northwest Laboratory, Richland, WA, 1981.

APPENDIX E.S

~~DEVELOPMENT OF A METHOD FOR~~ CHARACTERIZATION OF REDOX CONDITIONS IN BACKFILL AND WATER-ROCK SYSTEMS

ABSTRACT

The redox conditions (oxidation-reduction parameters) of the groundwater reflects the oxidizing or reducing condition of the natural environment. In a nuclear waste repository the redox conditions of concern are the oxidation or redox potential (Eh), the redox stabilizing (buffering) effect, and the limiting rates of reaction in reestablishing equilibrium after the disturbance created by construction of a repository. The redox potential of the groundwater will determine the oxidation state (valence) of multivalent radionuclides and the redox capacity is a measure of the resistance to change in the oxidation state of the system. In general, the solubilities of these radionuclides are lower and the sorption and retardation greater in a reducing environment.

In theory the redox potential of natural waters is both measurable and calculable using thermodynamic data and the analysis for the chemical species existing in the oxidized and reduced forms. In practice, it is a difficult task and no single measuring or calculational method can be relied upon.

Natural systems are frequently not in complete equilibrium and some knowledge of the kinetic behavior of the system becomes necessary in establishing system bounds. Understanding of natural systems results from characterizing the various mineral assemblages that determine oxygen fugacity that strongly effects the redox potential, multiple application of the various methods for determining the redox potential, and construction of Eh-pH, a stability field, diagrams which are graphical representations that bound the regions of stability for chemical species in aqueous solution and possible solid phases as a function of the system parameters Eh and pH.

Experimental and thermodynamic methods of redox conditions determinations are discussed in this appendix along with the general uncertainties involved in the application to nuclear waste repositories.

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INTRODUCTION

Knowledge of the Eh (and pH) of repository groundwater and the controls) on these parameters is a necessary part of site characterization because:

- -- Eh of the groundwater is an important aspect for the control of multivalent radionuclide oxidation state.
- Oxidation state of multivalent radionuclides determines the possible species that it may form with various ionic constituents of groundwater either natural or introduced from the waste package.
- The radionuclide species in the groundwater controls solubilities of radionuclides and solubility is a major control on radionuclides movement to the accessible environment.
- The radionuclide species in the groundwater is an important factor in sorption of radionuclides. Sorption is an important process retarding movement of radionuclides to the accessible environment.

Because of the importance of Eh and the generally recognized problems with its measurement, calculation and interpretation, it is important that NRC present DOE with its position on the fundamentals and relevance of redox conditions to repository siting. Appendix S presents NRC's position as it now stands.

1.1 Background

The nature of the chemical reactions between the various materials in the near-field strongly influence the mobilization and transport of the radionuclides from the repository into the surrounding host rock. Additional reactions (including precipitation with possible colloid formation) occur with the primary and secondary minerals of the cooler far-field rocks. Depending on the geochemical conditions at any time, different chemical forms of the elements are possible. One of the most important set of geochemical parameters constitute the redox conditions (ability of the environment to cause oxidation or reduction of a chemical species) of the system since the chemical speciation of polyvalent elements includes the possible formation of different oxidation states with markedly different solubility and sorption behavior. The primary redox parameter is the Eh,

which is an indicator of the ability of the geochemical environment to cause oxidation or reduction reactions. Other relevant parameters include temperature and poisoning (the resistance of the geochemical environment to change). Consequently, the geochemical conditions that will affect the oxidation states of the waste radionuclides must be sufficiently characterized and understood to make a projection into the future that will permit a more confident prediction of repository performance.

1.2 Government Regulatory Framework

1.2.1 Role of U.S. Agencies

1.2.1.1 DOE -

The DOE is responsible for the technical research and development necessary to identify a safe repository site and for construction and operation of the site after approval by the NRC.

1.2.1.2 NRC -

The NRC is responsible for reviewing and approving the DOE repository site development and issuing the appropriate construction and operating licenses consistent with regulations governing high level radioactive waste repositories.

1.2.1.3 EPA -

The EPA is responsible for the protection of the environment, including protection from radioactivity releases, and for the issuance of suitable regulations and requirements.

1.2.2 Relevant Sections of Draft NRC Technical Criteria (10 CFR 60)

§ 60.113 Content of application

(c) The Safety Analysis Report

(1)(ii)(c) An evaluation of the performance of the proposed geologic repository for the period after permanent closure, assuming anticipated processes and events, giving the rates and qualities of releases of radionuclides to the accessible environment as a function of time; and a similar evaluation which assumes the occurrence of unanticipated processes and events.

§ 60.113 Performance of particular barriers after permanent closure

(b)(3) The geochemical characteristics of the host rock;

§ 60.122 Siting Requirements

(b) Favorable Conditions

(4) Geochemical conditions that -- (i) promote precipitation or sorption of radionuclides; (ii) inhibit the formation of particulates, colloids, and inorganic and organic complexes that increase the mobility of radionuclides; or (iii) inhibit the transport of radionuclides by particulates, colloids, and complexes.

(c) Potentially adverse conditions

- (9) Ground water conditions in the host rock, including chemical composition, high ionic strength or ranges of Eh-pH, that could affect the solubility of the waste form or chemical reactivity of the engineered barrier system so as to increase the difficulty of designing the engineered barrier system to meet the performance objectives of Sects. 60.112 and 60.113.
- (10) Geochemical processes that would reduce sorption, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system.

§ 60.135 Requirements for the waste package and its components

- (a)(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 FUNDAMENTALS AND RELEVANCE OF REDOX CONDITIONS

Radionuclides transferred from the waste packages into the backfill and basalt environment may be retarded from transport toward the accessible environment by reactions with constituents of backfill and host rock minerals. Among the radionuclides generally recognized as critical to site performance, several (for example Pu, Np, U, Cm, Tc, I, Se, Sn, Pd, Ni) are capable of forming more than one oxidation state (valence) within

the range of redox conditions that may be expected. Some of these elements exhibit markedly different sorptive and solubility behavior for different oxidation states. Consequently, an understanding of the redox status along a flow path to the biosphere is an important parameter in the performance assessment of a waste repository.

2.1 Issue: Redox Conditions and Radionuclide Mobility

The primary issue to be addressed is the effect of backfill/host rock/groundwater components on the oxidation state of waste radionuclides and the consequences of forming particular oxidation states in terms of the solubility and adsorption behavior of the radionuclides as controls on their mobility.

2.1.1 Redox conditions

The redox conditions of concern are the oxidation or redox potential (Eh), the redox stabilizing (buffering) effect, or "poising", and the limiting rates of reaction in reestablishing equilibrium. Poising or Eh buffering is analogous to the buffering effect associated with the acidity of solutions (pH). In natural systems in equilibrium contact with the atmosphere, Eh is poised by reactions involving elemental oxygen. In the deep groundwater of the Grande Ronde basalt, the Eh and poising is probably controlled by oxidation-reduction reactions involving mostly iron-bearing minerals. In general, buffering (either pH or Eh) may result from maintaining the concentration (more precisely thermodynamic activity) of one of the controlling components at an approximately constant level during fluctuations in the

system. This is generally achieved by means of a chemical equilibrium which can absorb or generate the buffered component and compensate for undesired addition or removal of it by external means (see Fairbridge, 1972, for a more detailed discussion of buffered geologic systems).

The redox conditions (as well as pH) are determined by the chemical species present in the aqueous phase. Adjacent or intermixed solid mineral phases act as the external reservoir or sink to control the aqueous phase. In principle, the Eh and pH can be separately calculated if the system is at equilibrium and the chemical speciation is completely defined. In natural systems, complexity makes such a procedure less reliable. For non-equilibrium conditions, the calculation is never practical (except for simple systems in the laboratory) because the kinetics of all the reactions need to be understood and the reaction rate constants determined as a function of temperature and pressure.

Many redox reactions involve hydrogen ions (which is the case for water flowing through a waste repository) and the Eh and pH can be related through the Nernst equation if the activities of the other reacting substances are specified and the system is at equilibrium. A graph can then be constructed with pH as the abscissa and Eh as the ordinate that shows the boundaries of the stability fields for the species being considered.

A brief discussion of the oxidation-reduction processes are given in the following sections, and a detailed discussion of the thermodynamics of natural water systems (including Eh and pH and their effects) are presented by Pourbaix (1949), Garrels and Christ (1965), Krauskopf (1967), Fairbridge (1972), Stumm and Morgan (1981), and by Rydberg (1981).

2.1.2 Equilibrium Redox Fundamentals

The chemical processes of oxidation and reduction involve the electrons in the chemical bonds between atoms or ions with the loss of an electron constituting oxidation or a gain, reduction. This is conceptually analogous to acid-base reactions where protons (hydrogen ions) are transferred. Both oxidation-reduction and acid-base reactions are fundamentally electrical processes and both effects can be measured as a voltage difference between suitable electrodes.

The relative ease of oxidation or reduction of any chemical depends on the orbital electron arrangements. Noble metals, such as platinum and gold, are normally found in the elemental state since they are relatively stable toward oxidation. The more reactive metals, such as sodium and potassium, normally exist in the oxidized state as metal salts, are resistant to reduction. This difference in behavior forms the basis of the electrochemical series, which ranks metallic elements in order of the ease displacing from their solutions the ions of any element listed below them. The element going into solution would be oxidized and the one displaced (precipitated) would be reduced.

The same concept has been applied to non-metallic elements, ions, and compounds, and quantified on the basis of the electric potential generated by a solution of the particular species. A large number of measurements of oxidation couples (oxidized and reduced valence states of the species comprising a half cell) have been made and have been collected and listed by Latimer (1952), Krauskopf (1965) and Baas Becking et al (1960) for

natural environments. All potentials are referred to the standard hydrogen electrode that is assigned an arbitrary zero voltage. The sign convention is arbitrary; two conventions have been used, causing some confusion. The more recent geochemical literature (Stumm and Morgan, 1981) has adopted the International Union of Pure and Applied Chemistry (IUPAC) that lists the half-cell equation with the reduced species on the left and a negative sign for voltages more reducing than the hydrogen electrode and a positive sign for more oxidizing. Analogously to electrochemical series for metals, the reduced form of any couple will tend to react with the oxidized form of any couple below it, but not with any above it.

2.1.2.1 Acidity (pH)

Hydrogen ions are involved in many aqueous reactions. Because measurement techniques are relatively well developed and accurate, the activity of the hydrogen ion measured whenever possible in order to provide a common reference activity for a variety of reactions. (In dilute solutions, the activity is numerically equal to the concentration.) Also, because activities are frequently represented as logarithmic functions and used in logarithmic form in some thermodynamic calculations, the term pH was developed and defined as the negative logarithm (base 10) of the hydrogen ion activity.

At room temperature, a pH of 7 corresponds to neutrality, but at higher temperatures the neutral value decreases because of shifts in the ionization constant of water K_w . pH neutrality is defined as $1/2 \text{ p}K_w$ where $\text{p}K_w$ is $(a_{H^+})(a_{OH^-})$. At 200°C, neutrality corresponds to a pH of approximately

6.5. For a 1N solution of a strong acid, $\text{pH}=0$ and for a 1N solution of a strong base, $\text{pH}=14$. In nature, observed pH's lie mostly in the range of 4 to 10.

Measurements of the pH of groundwaters sampled from the Grande Ronde Basalt (the following discussion is taken from Smith et al., 1980) indicate that the pH at 45°C is approximately 10.1. Extrapolating to higher temperatures that would exist at waste disposal horizon indicates that the pH at 65°C lies between 9.4 and 9.9. The high values for the Grande Ronde groundwaters are consistent with groundwater isolated from the atmosphere and in contact with silicates and/or carbonates (Krauskopf, 1967). At elevated temperatures, two further processes affect pH: formation of clay minerals by alteration of primary minerals and hydrolysis of silicates. Clay formation accelerates as the groundwater is heated, resulting in a decrease of pH because of the consumption of the hydroxyl ion (OH^-) and generation of the hydrogen ion (H^+). The hydrolysis of silicates involves the production of clay minerals by a solid-liquid reaction, which causes a pH rise. The two reactions occur at different rates and have opposing effects, and the combined result is a complex variation of pH with time.

Hydrothermal experiments reacting natural waters with basalt showed an early pH depression as the clay minerals precipitated from the heated water. Later precipitation slows and the dominant effect is produced by the hydrolysis reaction. The characteristic result is an initial rapid drop in pH followed by a slower rise that asymptotically approaches steady state. The

extent of the pH depression was dependent on temperature, water composition, and the water/solid ratio. It was determined that the minimum possible pH in a repository at the Hanford site would exceed 3. It is expected that future work will cause an upward revision of this lower bound because it was based on seawater/basalt relations (Smith et al., 1980).

In addition to the need to know pH in the construction of pH-Eh diagrams to bound stability regions for different species, models developed for calculating the Eh of the basaltic groundwaters at the Hanford DOE site are pH-dependent (Smith, et al., 1980).

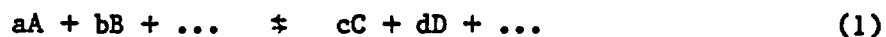
2.1.2.2 Redox Potential (Eh)

Redox potentials (Eh) can be calculated from thermodynamic considerations for redox couples (chemical species existing in two valence states within a system) provided that the activities and the Gibbs Free. Energy of formation of the components are known. The activity is numerically equal to the concentration only in infinitely dilute solutions. The activity will vary with temperature and concentration of the components and the determination of the necessary activities will involve considerable experimental work.

Natural systems usually contain more than one redox couple which can equilibrate at a potential corresponding to the dissolved species if equilibrium exists. No meaningful measurement or calculation can be performed for nonequilibrium systems.

The slowly changing environment, along with any radionuclides and their repository species, adds to the difficulty of Eh determination because of possible kinetic effects. It is possible that a single couple, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$, will predominate and make calculations more practical in a particular system.

The fundamentals of the Eh calculations are outlined below (see Rydberg, 1981, for details of the derivation of the equations). The change in the Gibbs free energy of formation of the chemical species in speciated system can be related to the redox potential of that system. The free energy of formation cannot be precisely defined without the use of thermodynamic equations and concepts; it may be considered a measure of the tendency to react. If the change in free energy (ΔG) is zero, the system is at equilibrium. If negative, the reaction will occur spontaneously, but the rate may be so slow that no reaction is perceptible. When ΔG is positive, an external energy source is required to drive the reaction. The magnitude of the ΔG serves as a measure of how far a mixture of species is from equilibrium; obviously, it must have some simple relation to the equilibrium constant, which is the ratio of the specific reaction rate constant in the forward direction to that in backward direction for a system in equilibrium. The equilibrium constant can shift to favor either direction depending on the perturbations to the system and asymptotically approach a new constant value. Consider the following general chemical reaction:



where A, B, etc. are the chemical formulas and a, b, etc. are the element balancing coefficients necessary for mass conservation.

The free energy change (kcal/mol) is given by

$$\Delta G = \Delta G^\circ + RT \ln \frac{[C]^c [D]^d \dots}{[A]^a [B]^b \dots} \quad (2)$$

where the brackets indicate activity and

R = ideal gas constant, 1.99 kcal/mol K,

T = absolute temperature, K, and

ΔG° = standard Gibbs free energy, kcal/mol.

In addition, at equilibrium

$$\Delta G^\circ = -RT \ln K \quad (3)$$

where K = equilibrium constant (based on activity).

The relationship between the reaction potential (voltage) and the free energy change is

$$\Delta G = -nFE \quad (4)$$

where

n = number of electrons transferred from one atom to another.

F = Faraday constant (96,500 coulombs or 23.1 kcal/volt), and

E = potential difference for a reaction. Labelled E° for standard state and Eh for redox potentials.

Combining Eq. (2) and Eq. (4) produces the Nernst equation for calculating the redox potential.

$$E_h = E^\circ + \frac{2.303 RT}{nF} \log Q \quad (5)$$

where Q = activity quotient [bracketed term in Eq. (2)].

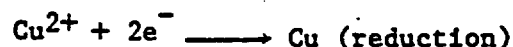
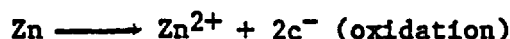
For reactions at 25°C, the combination of the constants give

$$E_h = E^\circ + \frac{0.059}{n} \log Q \quad (6)$$

The standard potential for a reaction may be obtained by subtracting potentials for the appropriated half-cell or electrode reactions that have been tabulated (all are referred to the H_2-H^+ half reaction) or from the free energy relationship of Eq. (4).

As an example, consider the displacement of the copper ion by zinc from a copper sulfate solution.

The half-cell reactions are:



which in addition gives the total reaction,



The tabulated values (Krauskopf, 1967) for the oxidation reaction is -0.76 and the reduction reaction, -0.34; consequently,

$$E_h = -0.76 - (-0.34) = -0.42.$$

The free energy change is

$$\Delta G (\text{reaction}) = \Delta G(Zn^{2+}) - \Delta G (Cu^{2+}).$$

The free energy of an element is zero and $\Delta G(\text{Zn}^{2+}) = -35.2$ kcal and $\Delta G(\text{Cu}^{2+}) = 15.5$ kcal (Krauskopf, 1967). Therefore,

$$\Delta G(\text{reaction}) = -35.2 - (-15.5) = -19.7 \text{ kcal}$$

and from Eq. (4) for $n = 2$,

$$E_h = \frac{-19.7}{2 \times 23.1} = -0.43.$$

2.1.2.3 Effective Electron Activity (pE)

Rather than use the Nernst equation to calculate redox potentials, some authors have chosen pE [Sillen (1967) and Stumm and Morgan (1981) for example] which is directly analogous to pH. The pE is operationally defined as the negative logarithm of the effective electron activity in solution.

Consider the following reduction (half) reaction written in general terms.

Oxidized species + $ne^- \longrightarrow$ reduced species with a corresponding activity quotient defined as

$$Q = \frac{[\text{Red.}]}{[\text{Ox.}][e^-]^n} \quad (6)$$

Combining Eq. (5) and Eq. (6) and splitting the $\log Q$ into two parts, we have

$$E_h = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Red.}]}{[\text{Ox.}]} - \frac{RT}{F} \ln [e^-] \quad (7)$$

For the reference hydrogen electrode,



By convention, $E^\circ = 0$ and the activities of H_2 and H^+ are unity.

Therefore, for the hydrogen reference scale, the potential is

$$E_h = - \frac{RT}{F} \ln [\text{e}^-] . \quad (9)$$

If we define $pE = -\log [\text{e}^-]$ and evaluate the constants, at 25°C

$$E = 0.059 pE \quad (10)$$

Combining Eq. (7) and Eq. (10), we get

$$pE = (\log K)/n \quad (11)$$

Therefore, all reactions involving electrons can be assigned a pE° value based on Eq. (11). Such relative electron affinities have been provided (e.g., by Stumm and Morgan, 1981) and can be used instead of $\log K$ for comparative purposes.

2.1.2.4 Eh-pH Diagrams

The Eh-pH, or stability-field, diagrams used in geochemical applications are graphical representations that bound the regions of stability for chemical species in aqueous solution and possible solid phases as a function of the measurable (or calculable) system parameters Eh and pH. The convention in constructing these diagrams is to plot calculated values

from the Nernst equation [Eq. (6)] vs pH; the latter as the abscissa and Eh as the ordinate. The pE (Sect. 2.1.2.3) may also be used in place of Eh with the same result since these two quantities are proportional to one another. A collection of these diagram and discussion of their construction and uses was first published by Pourbaix (1946) in relation to the corrosion of metals. The application to geochemical systems was recognized and became widely used to determine by graphical means the domains of relative predominance of dissolved species and the relative stability of coexisting solid substances. Many Eh-pH diagrams are available for geochemical systems. The construction and interpretation of a large number of these diagrams are covered in publications by Garrels and Christ (1965), Stumm and Morgan (1981), and Rydberg (1981).

These diagrams can be very complex depending on the number of solution species and solid minerals involved. The boundaries of the stability fields, and in some cases the identity of the chemical species and solids, shift with temperature and pressure. Consequently, a large number of Eh-pH diagrams are needed to understand and characterize a geochemical system. Because of the many species that can exist in groundwaters, a complete characterization of the geochemical behavior of the system is difficult if not impossible. However, they are still very useful in limiting the possible number of species and minerals that are effective in controlling the geochemical behavior and showing the general region of predominance.

In discussing examples of these diagrams we first consider water alone because of its importance in bounding the range of natural Eh and pH

values. The strongest oxidizing agent normally found in nature is atmospheric oxygen. Stronger oxidizing agents cannot persist in equilibrium with water because they would react (oxidize) with water and liberate oxygen. Similarly, materials that are stronger reducing agents than hydrogen gas cannot persist in nature because they will react to reduce water to produce hydrogen gas.

Consider the oxidation reaction



The Nernst equation [Eq. (6)] for this reaction is

$$E_h = 1.23 + \frac{0.059}{4} \log (\text{O}_2)(\text{H}^+)^4 \quad (13)$$

since $E_0 = 1.23 \text{ V}$ (tabulated value) and the activity of a liquid compound is unity by convention.

The pressure of oxygen in the atmosphere is 0.21 atm; consequently, Eq. (13) can be written as

$$E_h = 1.23 + 0.03 \log (0.21) + 0.059 \log (\text{H}^+) . \quad (14)$$

Since by definition, $\text{pH} = -\log(\text{H}^+)$, the equation for the upper limit of the redox potential for natural groundwaters becomes

$$E_h = 1.22 - 0.059 \text{ pH} . \quad (15)$$

Actually measured redox potentials in nature are always below those calculated from Eq. (15). A more realistic upper bound (Baas Becking et al., 1960) is

$$Eh = 1.04 - 0.59 \text{ pH} \quad (16)$$

The lower limit of the redox potential is represented by the hydrogen electrode reaction,



The Nernst equation for this reaction is

$$Eh = 0.0 + \frac{0.059}{2} \log (H^+)^2 - \frac{0.059}{2} \log (H_2) \quad (18)$$

Since the maximum pressure that hydrogen gas can attain is 1 atm, the equation for the lower limiting redox potential becomes

$$Eh = 0.059 \text{ pH} \quad (19)$$

Natural groundwater normally range from a pH of four to around ten. The lower value usually results from atmospheric carbon dioxide, humic acids and some soils. Higher pH's near ten result from CO₂ free water in contact with carbonate rocks and values to nearly 11 can result from interaction with silicates (such as basalt).

A graphical representation (from Rydberg, 1981) of these natural limits in relation to some redox couples for potential waste canister materials is shown in Fig. 1.

The next step in understanding and characterizing the geochemical behavior of groundwater is to construct similar diagrams with additional components.

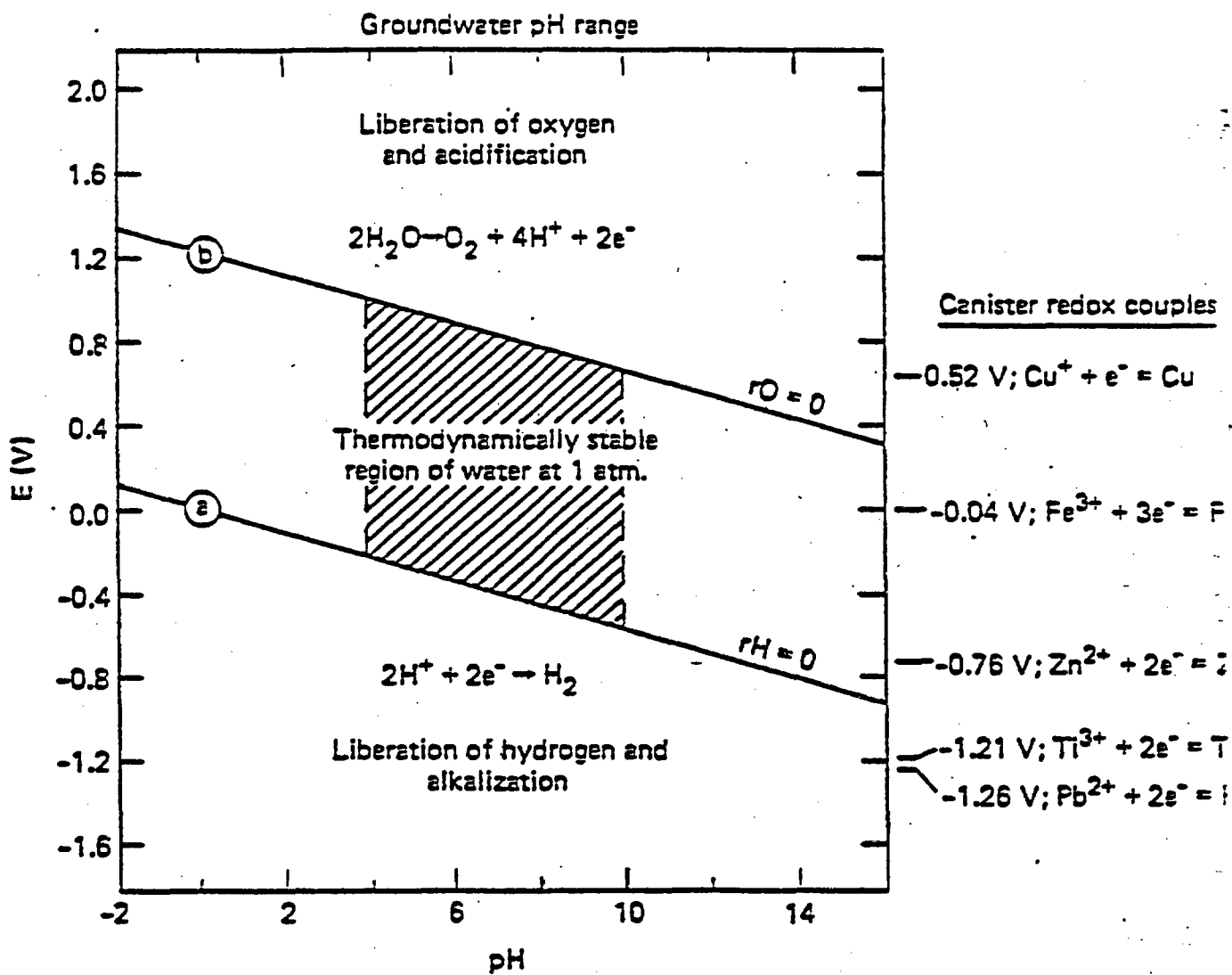
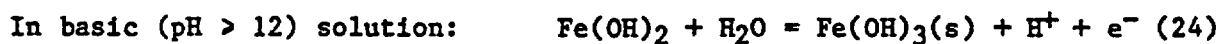
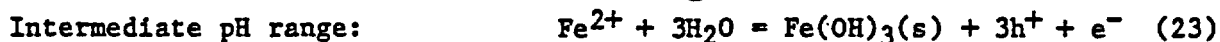
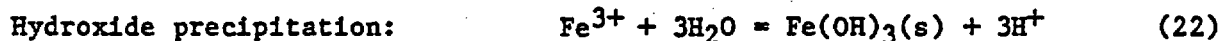
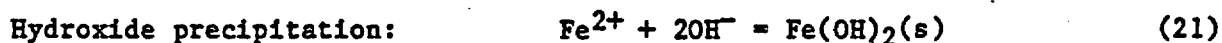
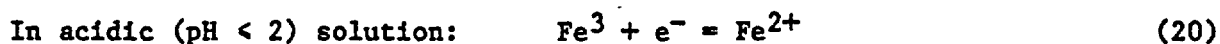


Fig. 1. Domain of thermodynamically stable groundwater (shaded area) and some water-canister redox couples at $[\text{H}^+] = 1 \text{ M}$. (From Rydberg, 1981.)

An important redox couple in many natural groundwaters is $\text{Fe}^{2+}/\text{Fe}^{3+}$.

Rydberg (1981) constructed an iron-water diagram (along with others) and interpreted it with respect to corrosion of a waste canister. The following discussion is taken almost verbatim from Rydberg (1981). The simple water system is complicated by the addition of iron species. In considering this complication, we shall make a number of simple assumptions about the iron system, which permit us to arrive at an approximately correct picture of this system. The reader is referred to Rydberg's paper for a discussion of a more complicated iron-water system.

Since our pH scale spans the alkaline side, the formation of iron hydroxides must be considered. We shall assume that they are of the simple form $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. We then consider the iron species Fe^{2+} , Fe^{3+} , $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, and the relations between them given below (Reactions 20-24).



It is well known that Fe^{3+} easily hydrolyzes and may precipitate out at pH as low as 3, while Fe^{2+} does not precipitate until pH 7 is exceeded. This motivates the formulation of reactions (20)-(22) even at neutral pH, where Fe^{2+} is stable and $\text{Fe}(\text{OH})_3$ has precipitated, we must have a redox equilibrium. This is also true in alkaline solutions, where most of both Fe^{2+} and Fe^{3+} have precipitated out; there are always dissolved species

(even at unmeasurably low concentrations). Each of these reactions is governed by an equilibrium relation. Use of the thermodynamic data from Pourbaix (1946) produced each of the following equations from the corresponding equation above.

$$E = 0.771 + 0.059 \log [\text{Fe}^{3+}]/[\text{Fe}^{2+}] \quad (20b)$$

$$\log [\text{Fe}^{2+}] = 13.29 - 2\text{pH} \quad (21b)$$

$$\log [\text{Fe}^{3+}] = 4.84 - 3\text{pH} \quad (22b)$$

$$E = 1.057 - 0.177\text{pH} - 0.059 [\text{Fe}^{2+}] \quad (23b)$$

$$E = 0.271 - 0.059\text{pH} \quad (24b)$$

These equations allow us to construct the potential-pH diagram of Fig. 2. We now describe the construction steps and begin with the relations which must be valid at pH 0 and pH 14. From Eq. (20), we can draw an iso-concentration line (i.e., $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$) from pH 0 at $E = 0.771$; we draw a horizontal line to pH 3, and then a dashed line (we do not know yet when Fe^{3+} starts to precipitate). We also draw line (24b), beginning at pH 14, going up to pH ~ 9 , where we dash the line (we do not know yet when all Fe^{3+} hydroxide has dissolved). We then consider the solubility of the hydroxides; for this we must assume an iron concentration, and we choose 10^{-4} M (~ 5 ppm). This gives the lines (23b) and (24b), which we draw from top and bottom till they hit lines (20b) and (24b). We can finally draw the line for Reaction (24), which meets the crossing points of lines (20b), (22b) and (21b), at pH 3 and pH 9.

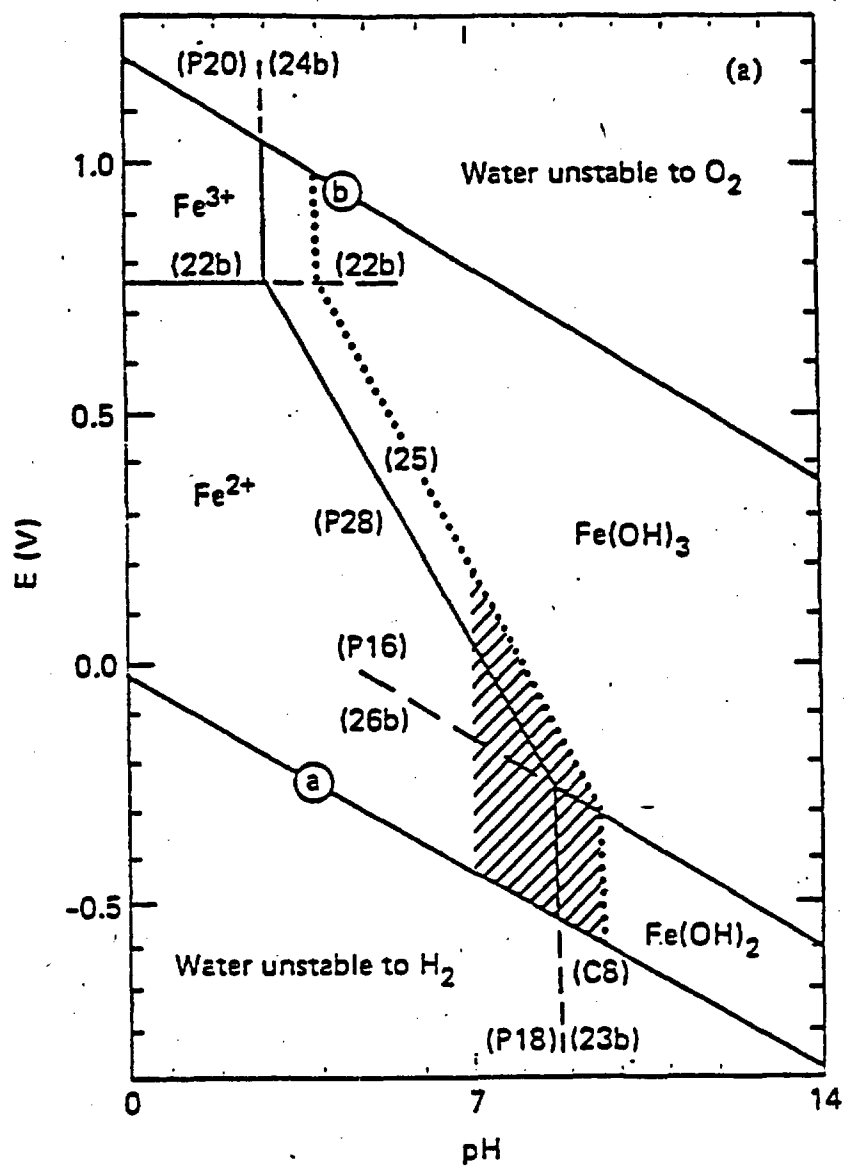


Fig. 2. The potential-pH diagram for iron-water. (From Rydberg, 1981.)

2.1.2.5 Relationship of Redox Potential and Oxygen Fugacity

Reactions of dissolved oxygen in groundwater with the country rocks will affect the redox potential (Eh) with some of these reactions creating a buffering effect (poising). Oxygen fugacity, which is an effective oxygen gas pressure in equilibrium with a solution is a convenient and measurable quantity in the laboratory for use in determining the oxygen activity in solution. When a gas behaves ideally, the fugacity is equal to the partial pressure. However, measuring oxygen fugacity in natural systems is not easy, but it is a convenient parameter that is calculable from equilibrium constants for oxygen-mineral reactions in thermodynamic equilibrium.

An excellent discussion of the geologic significance of oxygen buffering by mineral assemblages as a function of oxygen fugacity is given by Eugster and Wones (1962). Buffers in nature range from low to high oxygen fugacity. Examples include: quartz + fayalite + magnetite (QFM) (low oxygen fugacity) and magnetite + hematite (high oxygen fugacity) mineral assemblages. According to Eugster and Wones (1962), in examining the magnitude of the oxygen fugacity, it is convenient to distinguish three possible cases: the oxygen fugacity (f) is either: (1) internally defined and buffered; (2) internally defined, but unbuffered; or (3) internally undefined. The discussion of these cases below is taken directly from Eugster and Wones (1962). Case (1) is represented by any magnetite + hematite or QFM mineral assemblages since they define f for a given temperature and pressure. These assemblages are buffered (poised) in that they react to oxygen additions or losses (and hydrogen in the presence of water) by adjusting the ratio of the solids not by changing f . The

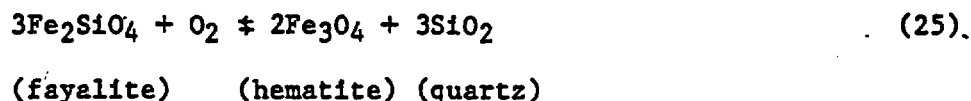
total buffering capacity depends on the amounts of solids present that participate in the redox reactions.

Any iron compound with a variable $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio, which includes a great majority of natural iron silicates, represents Case (2). Wustite is the only mineral of this type for which the relationship between the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio, f , and temperature has been determined experimentally. For a given temperature and pressure there is a direct correlation between the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio of the solid and the f of the vapor phase. Any change in f is immediately reflected by a change in the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio. Since this also holds for complex systems, the f of a mineral assemblage containing only one iron mineral can be defined by the existing $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio provided that experimental data are available. Such an assemblage has no buffering capacity and changes in f imposed by the surroundings will immediately affect the internal f and the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio.

If a mineral assemblage contains a single iron mineral with a fixed $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio, such as magnetite, the f is not defined internally (Case 3), although it is possible to give upper and lower limits. Such an assemblage is unbuffered to change in f that is imposed from without.

The important point made by Eugster and Wones (1962) is that the oxygen fugacities of a great many assemblages are defined and can be evaluated if the necessary data are obtained for natural and synthetic systems. Smith et al. (1980) developed an equation relating the Eh to

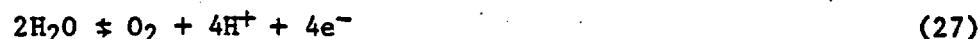
the oxygen fugacity from the QFM buffer, which is probably the Eh controlling iron-bearing mineral in basalt. As an example of this type relationship, we have outlined the derivation below. In a simplified form the reaction with the dissolved oxygen may be written as



The equilibrium constant is

$$K = \frac{[\text{Fe}_3\text{O}_4]^2 [\text{SiO}_2]^3}{[\text{Fe}_2\text{SiO}_4]^3 [\text{O}_2]} = \frac{1}{[\text{O}_2]} = \frac{1}{f} \quad (26)$$

where the bracketed expressions are activities, which are unity for the solid minerals. It is customary to use fugacity with units of pressure in place of the oxygen activity. Theoretically, that is incorrect since activity is always related to a standard state of unity and is dimensionless; however, it is numerically correct because the activity is the ratio of the fugacity (in atm) at a given temperature that of a standard state, which for gases is 1 atm. A numerical result for the equilibrium constant, K, can be calculated from the Gibbs relationship [Eq. (3)] using tabulated thermodynamic data (Robie et al., 1978). The oxygen fugacity (f) can then be calculated by Eq. (23) for use in the equation relating Eh and oxygen fugacity which is developed below. The oxygen fugacity is related to Eh through the reaction describing the oxidation of water, i.e.,



The activity quotient (using f for oxygen activity) for this reaction [see Eq. (3)] is

$$Q = f [H^+]^4 \quad (28)$$

which when combined with the Nernst equation [Eq. (5)], the redox potential is

$$E_h = 1.23 + \frac{2.303 RT}{4F} \log f [H^+]^4 \quad (29)$$

since $E_h = 1.23$ for the reaction (see page U-20). Using the values for R and F , the definition of pH , and splitting the log term produces

$$E_h = 1.23 + 4.96 \times 10^{-5} (T) (\log f) - 1.984 \times 10^{-4} (T)(pH). \quad (30)$$

2.1.2.6 Mixed Redox Couples of Natural Waters

Redox reactions in natural systems are frequently irreversible and not at equilibrium, and the measured E_h is often a mixed potential resulting from several redox reactions that may not readily couple with each other. A meaningful E_h cannot be defined for such nonequilibrium systems. However, partial equilibrium may be approached in many cases and a metastable system may exist in which a working redox potential can be related to certain redox couples (Carnahan, 1982).

In theory, it is possible to evaluate the redox potential in natural waters by determining the relative activities of the members of some

(or all) of the redox couples present and then calculating an Eh for each couple from the Nernst equation. If the calculated Eh's for couple are equal, the system is at equilibrium and the calculated Eh represents the system Eh since an aqueous sample can exert only a single potential and the individual couples must speciate to produce the system voltage when in equilibrium. For example, Thorstenson and Fisher (1979) analyzed water from several wells in the Fox Hills-Bosal Hill Creek aquifer region in the Dakotas. Redox potentials calculated from components of the couples $\text{HS}^-/\text{SO}_4^{2-}$, CH_4/CO_2 , and NH_4^+/N_2 agreed to within about 50 mV, indicating that the redox reactions approached, but probably did not achieve true equilibrium. The calculated values were about 200 mV more negative than the Eh values measured with a platinum electrode (Carnahan, 1982).

Redox potentials calculated from the activities of the components of naturally occurring couples can be used to estimate the Eh of water samples, but may not be reliable in all cases. In any case, the method is useful for identifying controlling redox reactions (Carnahan, 1982).

Only a few elements (C, N, O, S, Fe, Mn) are normally predominant participants in aquatic redox processes (Stumm and Morgan, 1981).

Besides those previously mentioned, normally present redox couples in natural waters include: CH_4/CO_2 , $\text{H}_2\text{O}/\text{O}_2$, $\text{NH}_4^+/\text{NO}_3^-$, $\text{S}^{2-}/\text{SO}_4^{2-}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, and $\text{Mn}^{2+}/\text{Mn}^{4+}$.

In the basaltic waters of the BWIP site, CH_4/CO_2 and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couples seem likely candidates for the constituent analysis method for determining the Eh of water samples. The $\text{As}^{3+}/\text{As}^{5+}$ couple has been suggested as a good candidate for the redox potential characterization of the BWIP site groundwater (Rockwell-Hanford Operations, 1982) by addition of arsenic compounds to the groundwater and measuring the resultant ratio of $\text{As}^{3+}/\text{As}^{5+}$.

2.1.2.7 Effect of Redox Conditions on Solubility and Sorption of Radionuclides

The rate at which radionuclides are transported to the accessible environment will be determined by their solubility, the rate and path of groundwater movement and the sorption reactions of the radionuclides with minerals in the backfill, in fractures in the host rock, and in the host rock itself. An important parameter affecting both solubility and retardation reactions for multivalent radionuclides is the redox potential. A detailed discussion of solubility and radionuclide sorption is given in Appendices U and T, respectively. In this appendix the effects of the redox conditions on these parameters are only briefly discussed.

The oxidation states of the radionuclides will be largely governed by the redox potential of the groundwater with which they interact. The solubility and sorbability of many of the radionuclides that may be mobilized by the groundwater can exhibit markedly different geochemical behavior at different oxidation states (valences), particularly technetium,

selenium, and the actinides. The solubilities are generally lower for reducing environments (Apps et al., 1982) and the sorbabilities tend to be higher (Serne and Relyea, 1982).

For example, under the redox conditions for deep groundwater not in contact with atmosphere, the mobile TcO_4^- and NpO_2^- ions are not the stable oxidation states for the elements. Rather, insoluble TcO_2 and NpO_2 or related hydrated forms are expected to be the solubility controlling phases. This conclusion is based on available thermodynamic data and supported by experiments (Bondietti and Francis, 1979).

Several of the actinides can exist in various oxidation states depending on the redox potential of the solution. The possible oxidation states in aqueous solution of the actinides under mildly oxidizing or reducing environmental conditions are Ac^{3+} , Th^{4+} , U^{4+} , UO_2^{2+} , UO^{+2} , Np^{4+} , NpO^{+2} , Pu^{3+} , Pu^{4+} , PuO_2^+ , Am^{3+} , and Cm^{3+} (Apps et al., 1982). Actinide ions, regardless of valence tend to form complexes in aqueous solution with some of the various anions found in groundwater, which complicates estimating the solubility of the actinides even when Eh is fixed and known.

Once the groundwater contacts and transports radionuclides away from the repository, a major mechanism for preventing or retarding radionuclide movement will be sorption (on the basalt and on the secondary minerals in the fracture). The oxidation state along with complex formation and, consequently the redox potential, was

identified as a key variable in nuclide retardation by Ames and Rai (1978) and Rai and Serne (1978) for several long-lived isotopes such as ^{239}Pu , ^{238}U , ^{237}Np , ^{79}Se and ^{99}Tc . Earlier studies neglected to measure or consider the redox potential in interpreting their results. It seems that knowledge of the redox potential would be unnecessary provided that the solution species and solid phases were completed and the various sorption mechanisms understood. Since complete characterization of a complex system is not possible, the redox potential serves to reduce the need for a detailed characterization by substituting a resultant effect that is measurable.

In a recent review of the status of radionuclide sorption-desorption studies performed by the Waste Rock Interaction Technology (WRIT) program, Serne and Relyea (1982) conclude the following:

"Experimental studies of redox mediated nuclide retardation have concentrated on three multivalent elements Tc, Np and Pu. It appears that dominant solution redox couples such as $\text{Fe(II)}-\text{Fe(III)}$ can cause reduction of nuclides and removal as insoluble precipitates. Thermodynamic calculations based on measured $\text{Fe(II)}-\text{Fe(III)}$ solution concentration in laboratory experiments predict that for igneous rocks such as basalt and granite reduction of Tc(VII) , Pu(V or VI) and Np(V) should occur. Experimental results do show significantly reduced nuclide solution concentrations. It appears that Tc(VII) reduction forms Tc(IV) hydroxide precipitates and it is reasonable to surmise that Pu and Np would also. In addition some laboratory studies are described in which the reduction of Pu appears to occur at

the solid/solution interface even though the bulk solution is oxidized. Minerals with large percentages of structural Fe(II) appear to reduce the plutonium in a heterogeneous solid/solution redox reaction."

2.1.3 Non-equilibrium Redox Conditions

The construction of a repository and the subsequent emplacement of waste packages will introduce perturbations in the geochemistry of the host rock in and around the repository. Introduction of atmospheric oxygen will tend to change the ambient redox condition from reducing to oxidizing. Mobilization of the components of the waste package by groundwater that will eventually interact with the repository system can also affect the redox conditions and transport properties of the radionuclides. It is generally known that for reducing conditions the metals that may constitute the waste package will resist corrosion and that the solubilities of the actinides are usually much lower. The sorption of radionuclides on the minerals of the host rock may also be decreased by increases in the redox potential (Sern and Relyea, 1981). Consequently, an understanding of the chemical and physical processes and the time scale involved in rate of return to the ambient redox conditions of the unperturbed state is a necessary adjunct to the information base required for the performance assessment of a repository. This involves both the near field and far field, with the former influencing the initial mobilization of the components of the waste package (including the radionuclides) and migration from the repository system, and the latter having the greater effect on retardation of radionuclides along the transport path.

According to Stumm and Morgan (1981), much progress has been made in understanding the mechanisms of redox reactions, especially how the changes in the state of coordination during the reaction are coupled to the changes in oxidation state. Many, if not most, redox reactions involve substitutional changes as an integral part of the overall process. As an example of the dramatic change that can occur in structural geometry and lability by the addition of an electron, Stumm and Morgan (1981) discuss the reduction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ to $\text{Cr}(\text{H}_2\text{O})_6^{2+}$. They pointed out that the reaction distorts the octahedral structure of the former by elongation along one axis which causes an increase in the water exchange rate between the complex and the solvent by a factor of 10^{15} . Although this particular reaction is not expected to be important to a repository, it represents an extreme case for a potential repository metallic constituent. Stumm and Morgan (1981) also discuss the experimental determination of rate constants and kinetic mechanisms for some simple systems for the oxidation of Fe^{2+} and Mn^{2+} and some sulfides which may have some applicability to understanding repository geochemistry.

An important parameter in determining the resistance to change in Eh is the redox capacity (strictly speaking, the reduction capacity). The redox capacity (ρ) at any Eh is defined as the quantity of strong reductant in moles that must be added to a liter of the sample solution to cause a lowering of the Eh by 1 volt (Nightingale, 1958), i.e.,

$$\rho = dC/d(\text{Eh}) \quad (31)$$

Actually, this represents the reciprocal of the slope at any point in a plot of the resultant Eh vs the cumulative amount of reductant (C) that is added to the sample. In well-poised and labile systems, ρ is large, and the system strongly resists changes in Eh, and Eh measurements are relatively easy and reproducible (Langmuir, 1971). The opposite is true for low values of ρ . Natural groundwater systems with substantial concentrations of organic materials tend to be poorly poised. Natural waters that are high in iron content tend to be strongly poised. However, the BWIP groundwater does not appear to be well poised because of the low iron and sulfide content (Benson, 1978). The concept of redox capacity may be illustrated in terms of the $\text{Fe}^{++}/\text{Fe}^{++1}$ couple (Langmuir, 1981) for which the Nernst equation at 25°C is

$$\text{Eh} = 0.771 + 0.059 \log [\text{Fe}^{3+}]/[\text{Fe}^{2+}] . \quad (32)$$

The redox capacity is greatest when $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$ and the total iron concentration is high. The system is poorly poised (ρ small) when $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ is less than 10^{-5} or greater than 10^5 , or when both $[\text{Fe}^{3+}]$ and $[\text{Fe}^{2+}]$ are less than 10^{-6} molar.

Stumm (1966) describes redox capacity in terms of the net current, which is zero at equilibrium. In poorly poised systems the net current is close to zero for a wide range of Eh values in the vicinity of equilibrium, which frequently prevents meaningful Eh measurements.

A crude guess by Smith et al. (1981) of the time required to bring the repository back to near the initial geologic equilibrium is hundreds of years. However, a sound basis for the estimate needs development.

Alteration of basaltic components along fractures and fissures and the formation of secondary minerals should provide clues to the Eh controlling reactions. It may be possible to estimate the potential rates of reaction from the degree of alteration and the rates of flow of groundwater through the system and from laboratory determinations.

2.1.4 Redox Conditions Summary

Redox conditions represent the oxidation or redox potential (Eh), the redox stabilizing effect (poising) and the limiting rates of reactions in reestablishing equilibrium conditions.

The redox potential is the measured (in volts) of the tendency of a substance to be oxidized or reduced, i.e., change the oxidation or valence state of a chemical specie by the removal or addition of an electron in the outer shell.

In the deep groundwater of the Grande Ronde Basalt, the Eh is controlled primarily by the oxidation - reduction reactions involving iron-bearing minerals which results in a reducing environment that is a more favorable condition than an oxidizing environment in regard to resisting corrosion of metals, lowering the solubility, enhancing sorbability of the long-lived radionuclides.

In equilibrated systems, the redox potential (measured in volts) can be calculated from thermodynamic data and the activities (effective concentrations) of the reacting species by the newest equation. These redox potentials are the difference between the potential from the reacting species and the standard hydrogen electrode, which is

arbitrarily assigned a zero potential tables of the potentials from various oxidation reactions for a single species (half-cell reaction) have been prepared and arranged in order of descending oxidizing power with the one having the greatest oxidizing power at the top and the lowest (or greatest reducing power) at the bottom. Those above the hydrogen reaction (electrodes) are oxidizing and are arbitrarily assigned a positive sign; those below are reducing and are assigned a negative sign. By algebraic addition of these potentials, standard redox potentials for selected reactions can be obtained.

In aqueous systems, the Nernst equation also relates the Eh to the pH (measure of the hydrogen ion activity or concentration). This permits construction of Eh-pH diagrams, which are graphical representations that bound the regions of stability for the chemical species and possible solid phases. The convention is to plot Eh as the ordinate and pH as the abscissa. The complexities of natural systems and variations of Eh and pH with temperature and pressure present a complete characterization of the system by this means, but these diagrams are very useful in limiting the possible number of species and minerals that are effective in controlling geochemical behavior.

Construction of repository will introduce perturbations in the geochemistry of the host rock and any subsequent mobilization of the waste package components will add complexity to the system. The kinetics of reestablishing equilibrium conditions are too complex for complete characterization, but bounding of the problem may be possible. The resistance to change of the redox potential (poising) is an important

parameter in this respect. This resistance is measured in terms of the redox capacity, which is defined as the quantity of strong reductant in moles that must be added to a liter of the sample solution to cause lowering of the Eh by 1 volt. The higher the redox capacity, the greater the resistance to change. In iron-water systems, the redox capacity is greatest when the activity of Fe^{3+} equals the activity of Fe^{2+} and the total iron concentration is high.

Redox reactions in natural systems are frequently irreversible and not at equilibrium. However, partial equilibrium may be approached in many cases and a metastable system may exist in which a working redox potential can be related to certain redox couples (a simultaneous existence of an oxidized and reduced state of a chemical species). In theory, it is possible to evaluate the redox potential in natural waters containing mixed couples by determining the relative activities of some (or all) members of the couples and then calculating the Eh for each couple with the Nernst equation. If the calculated Eh's for the couples are equal, the system is at equilibrium and the calculated Eh represents the system value. In practice, this is very difficult to accomplish.

2.2 Information Requirements Concerning Redox Conditions

The purpose of this section is to indicate the information which should be supplied to the NRC concerning the characterization of redox conditions in the BWIP for the purpose of forming the basis for a NRC staff judgment as to the BWIP site characterization program adequacy, acceptability, and likelihood of success.

The areas in which the NRC staff requires information concerning BWIP redox conditions are as follows:

1. the general approach to information acquisition,
2. the types of information to be obtained,
3. plans for information acquisition, and
4. plans for information verification.

The following sections discuss these information requirements in more detail.

2.2.1 General Approach

It is necessary that the general approach to be taken in obtaining and using information related to redox conditions be specified at the outset. One aspect of this information is the place that redox conditions will occupy in supporting the license application anticipated in the future. Since redox considerations strongly affect other geochemical conditions and processes that will presumably be employed in the performance assessments (i.e., sorption and solubility), it is important to know which of these parameters will be relied on in the site characterization and/or license application and how the applicant will use information on redox conditions to support the values or bounds for these parameters.

It is also important that the repository project indicate the philosophical approach to be used in characterizing redox conditions. The types of considerations that should be elaborated on here are indicated by the following questions.

1. Will a bounding approach (e.g., the use of Eh-pH diagrams) be employed, implying that measurement of precise values may not be necessary, or will specific values be obtained, implying a need for determination of confidence bounds for the parameters?
2. Will data be obtained under expected, worst-case, anticipated, and/or unanticipated repository scenarios?
3. Will probabilistic arguments be employed, implying the need for probabilities on the redox conditions?
4. Will data be obtained at a variety of spatial locations (i.e., waste package interface, near-field, and far-field) or will bounding conditions be identified, supported and used?

The answers to these questions will strongly affect the evaluation of the ongoing repository characterization program and output since the data that might be entirely adequate under one approach may be clearly deficient under another.

2.2.2 Information Acquisition Requirements

As a result of the considerations described in Sect. 2.2.1, it is very difficult to specify the precise information requirements without knowing the overall approach to be taken in licensing the repository. However, it is still possible to outline much of what redox-related information needs to be acquired. The two general areas in which information must be supplied are (a) the types of data that need to be acquired and (b) the methods that will be used to obtain the data. Both areas are addressed below. In addition, a detailed discussion of methods for determining redox conditions is given in Sect. 2.3.

The types of redox-condition data that must be obtained can be separated into the following types:

1. the redox conditions in the unperturbed (or minimally perturbed) repository,
2. the redox buffering capacity (poising) of the unperturbed (or minimally perturbed) repository, and
3. the redox conditions under which radionuclide migration might take place for the scenarios defined in Sect. 2.2.1.

The redox conditions of the repository need to be determined in a condition as close to unperturbed as possible. This information is necessary as a benchmark for verification purposes as well as being the initial condition for evaluating the perturbations introduced by the repository.

The determination of redox conditions may include the following parameters: calculation or measurements of Eh, ionic strength, identification of soluble and insoluble species, pH and temperature, depending on the measurement methods employed and the general approach to the repository characterization (see Sect. 2.2.1). Adequate information should be developed to allow determination of whether the system is in equilibrium or is a mixture of unequilibrated couples.

Specific parameters of interest include oxygen fugacity and the $[\text{Fe}^{+2}]/[\text{Fe}^{+3}]$, $[\text{CH}_4]/[\text{CO}_2]$, $[\text{S}_4]/[\text{SO}_6]$, and $[\text{As}^{+3}]/[\text{As}^{+5}]$ redox couples.

The redox buffering capacity (poising) of the unperturbed repository is an important factor in the ability of the repository to reestablish

conditions relatively close to the unperturbed state after repository closure. A question of specific interest is the poisoning of the repository with respect to the oxygen introduced into the repository environment during the operational phase of the repository. If poisoning capacity is lower than currently anticipated, the repository may remain in a substantially more oxidizing condition than the anticipated maximum of a few hundred years, thus having a significant impact on radionuclide properties dependent on redox conditions (i.e., sorption, solubility). Identification of the redox couples responsible for repository poisoning and the concentrations of the species present in the couples in the unperturbed repository is clearly necessary to satisfy this information requirement.

The redox conditions under which radionuclide transport may be taking place are important in determining the solubility and sorption of the radionuclides. The relevant information here is the redox conditions at the time migration would take place under various postulated repository scenarios. These conditions will clearly be a function of the initial repository conditions and repository poisoning, as discussed above. Additionally, the perturbations introduced into the repository (e.g., temperature, radiation, backfill materials, canister materials, borosilicate glass) and the kinetics of the reactions of the initially oxygenated repository environment with the host rock, secondary minerals, and perturbations, will determine the redox conditions as a function of time. In order to properly determine the solubility and sorption of radionuclides during transport, the redox conditions must

be known or bounded as a function of space during the time of transport. Specific points that must be addressed include (1) the equilibrium redox conditions of the perturbed repository and (2) the rate at which equilibrium is attained.

It is recognized that this may be an extremely complex and large undertaking if it cannot be shown that the repository approaches a perturbed equilibrium condition in a relatively short time span.

However, the pivotal importance of redox conditions in determining the retardation behavior of many radionuclides requires that this information be provided or bounded to adequately characterize the repository geochemical parameters, and thus repository performance.

2.2.3 Information Acquisition Plan

It is necessary that the NRC staff know not the types of redox-conditions-related information that will be obtained and the plans to acquire the information in order to properly evaluate the adequacy of the BWIP repository characterization program in areas related to redox conditions. These plans include the specific types of data to be acquired to support the general characterization approach outlined in Sect. 2.2.1, the methods or experiments that will be employed to acquire the information, the schedule for acquisition of the information and the relationship of the various experiments to each other and the overall objectives in the redox conditions areas.

2.2.4 Information Verification

The adequate characterization of the redox conditions in a repository must not only supply information related to redox conditions, but also identify how the information will be verified as being relevant to and characteristic of the historical and future redox conditions in the repository. Specifically, the NRC needs to know what information will be generated or obtained to show that the calculations, laboratory experiments, and even in situ experiments represent "reality" for performance assessment purposes. Examples of questions to be addressed are "how are solubilities calculated with existing thermodynamic data bases to be shown to be either accurate or bounding for the BWIP?" or "how are sorption parameters measured under laboratory conditions to be shown to be relevant to the BWIP?" The

adequacy of the information gathered by the BWIP in support of their repository characterization is critically dependent on verifying data concerning redox conditions as being representative or bounding with respect to the actual situation.

2.2.5 Information Requirements Summary

The following items summarize the information required by the NRC staff to assess the adequacy and acceptability of the proposed BWIP site characterization activities concerning redox conditions:

1. General approach - information concerning how redox condition data will be used in the characterization and licensing of the BWIP site.
2. Information to be acquired - information concerning redox conditions in the unperturbed repository, the redox capacity of the unperturbed repository, and redox conditions under which radionuclide migration might take place following repository closure.
3. Information acquisition plan - what types of data related to redox conditions will be acquired; what acquisition methods will be employed; what is the schedule and relationship of redox information acquisition activities?
4. Information verification - how will the information related to BWIP redox conditions be verified as being representative or bounding with respect to the actual situation in the post-closure repository?

2.3 Methods for Determining Redox Conditions

The methods for measuring many of the relevant redox conditions are procedures that have been used for many years. The measurement of temperature is trivial and the calculation of temperature perturbations can be accomplished using well-known and proven techniques.

The measurement of pH can also be accomplished using proven techniques with known accuracies and limitations (Langmuir, 1971). The measurements of the concentrations of elements and ionic species is also a matter of standard chemical or radiochemical technique.

The central issue in determining redox conditions is how to determine the Eh of a geochemical system. When combined with the measurement of the parameters discussed above, the result would be the methodological ability to determine the relevant geochemical redox conditions, poising, and kinetic information. There are two classes of methods that can be employed to determine the Eh of a geochemical system: (1) direct measurements involving the use of electrodes, indicators, etc., and (2) indirect methods involving calculation of the Eh from thermodynamic principles or measuring the relative concentrations of ionic species in various redox couples and inferring the Eh. These aspects of Eh determination, as well as considerations about verification and quality assurance of the results, are discussed in the following sections.

2.3.1 Direct Methods for Determining Eh

There are two types of direct (experimental) methods for determining Eh: colorimetric methods and electrometric methods.

2.3.1.1 Colorimetric Methods

Colorimetric methods for determining Eh depend on the fact that certain chemical compounds (indicators) exhibit different colors when dissolved in aqueous solutions having different redox potentials. A summary of information on these techniques is given below. For more details, the reader is referred to (Langmuir, 1971) or (Zobel, 1946).

Indicators used in geochemical situations must (a) cover the appropriate potential range, (b) exhibit reversible behavior, (c) have a sharp color or fluorescence transition, and (d) be stable in aqueous solution. A variety of indicators has been developed that cover the range of Eh typical of geochemical systems. The use of colorimetric methods for determining Eh is not widespread as the result of apparent simplicity of electrometric methods.

Limitations concerning colorimetric methods are as follows:

1. The Eh range covered by a specific indicator is limited.
Therefore, it may be necessary to use several indicators to cover the range of interest.
2. Some indicators will react with the system under consideration in an undesirable manner (e.g., adsorption, chemical reaction), thus making the results invalid.

3. The use of colorimetric methods is ruled out in cases involving colored or turbid samples.
4. The indicator will have some capacity for electrons and protons. If the geochemical system under consideration is poorly poised, the indicator will alter the Eh of the system.
5. Obtaining in situ measurements generally involves withdrawing a sample of groundwater from the area of interest and then using the colorimetric indicators. The withdrawal process introduces opportunities for perturbing the sample chemistry to the point that the results may be meaningless.

It is appropriate to conclude that colorimetric indicators should not be solely relied on to give reliable results concerning Eh measurements in geochemical systems. However, they may be useful as a confirmatory measure in conjunction with other techniques.

2.3.1.2 Electrometric Determination of Redox Potential

Inert metal electrodes composed of platinum or of gold are used to estimate redox potential. An inert electrode is used in conjunction with a reference electrode to form a complete cell. Reference electrodes are usually mercury-calomel (Hg, HgCl) or silver-silver chloride (Ag, AgCl). The ideal inert electrode would be sensitive only to electron activity and would be equally sensitive to electrons from any half-cell. No real electrode fulfills these ideals in all chemical systems. Not only are real electrodes more sensitive to some half-cells than others, but also they are susceptible to surface

poisoning effects (Zobel, 1946) and to composite or "mixed" potentials (Stumm and Morgan, 1981).

Platinum electrodes are the most commonly used electrodes for Eh measurement. In relatively pure solutions in laboratory experiments, platinum electroplated (platinized) platinum electrodes provide large surface area, maximizing the exchange current and consequently, the responsiveness of the electrode. In field situations, however, the platinized platinum electrode is more susceptible to poisoning than bright platinum (Langmuir, 1971) and the latter is generally preferred. Even bright platinum electrodes are susceptible to poisoning due to the formation of surface oxide or hydroxide coatings (Watanabe and Devanathan, 1964). Sulfide, hydrogen, methane and carbon monoxide, as well as organic films, are also known to affect platinum electrode response (Langmuir, 1971). For this reason it is important to ensure that electrodes are kept clean and that they are frequently checked against a reference solution such as Zobel's solution (0.003 M potassium ferrocyanide and 0.003 M potassium ferricyanide in 0.1 M potassium chloride, $E_{\text{Zobel}} = 0.43$ at 25°C (Zobel, 1946). Garrels and Christ (1965) conclude that the most satisfactory cleaning method is abrasion with fine emery paper.

Formation of surface coatings may improve platinum electrode performance in some systems. For example, the formation of a ferric oxyhydroxide layer on platinum is said to catalyze the ferric oxyhydroxide-ferrous iron reaction and to enable the measurement of a stable reproducible Eh (Langmuir, 1971). Sillen (1966) suggested that

the spread in Eh values compiled by Baas Becking et al. (1960) were influenced by catalysis due to the presence of manganese oxides.

Gold electrodes are used less than platinum because they exhibit erratic potentials in sulfide-containing systems (Whitfield, 1969) and because the exchange current density on gold is lower than that on platinum (Whitfield, 1972). Morris and Stumm (1967) suggest that where exchange current density is less than 10^{-9} A cm^{-2} that Eh measurements are imprecise and that even below 10^{-5} A cm^{-2} it is difficult to obtain measurements which are in accord with Nernst theory. Whitfield (1972) found that none of five cells he studied (three freshwater-mud-minced meat; two seawater-mud) produced current densities above 10^{-7} A cm^{-2} and that with gold electrodes, only 10^{-9} A cm^{-2} was observed. In an extremely pure system, however, Watanabe and Devanathan (1964) reported a Nernst potential corresponding to the $2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ (Eh = 1.23 - 0.059 pH), but that the exchange current density was only 10^{-10} A cm^{-2} . On the other hand, Morris and Stumm (1967) report current densities as high as 10^{-4} A cm^{-2} in 10^{-3} M each for Fe^{3+} and Fe^{2+} .

Reference electrodes are also susceptible to poisoning by bromide or sulfide and may become clogged in suspensions of fine particulate matter. Langmuir (1971) suggests that reference electrodes be frequently checked and that if a reference electrode performance is not restored by changing the electrolyte, it be discarded.

In addition to the electrode-specific limitations included in the above discussion, there are two other major limitations to electrometric measurements. The first is that the Eh of poorly poised systems tend to drift over time and have very close to zero potentials over a wide range of Eh values in the vicinity of equilibrium. This consideration is especially relevant to the BWIP case since the system does not appear to be well poised (Benson, 1978) as a result of the low concentrations of iron and sulfide in Pasco Basin groundwaters. A second limitation is that the electrode measurements represent the net potential of the solution, which may be an equilibrium potential or the algebraic sum of the mixed potential from unequilibrated redox couples. Thus, the meaning of an Eh measured by electrometric methods is always open to interpretation unless other information is available.

As with the colorimetric methods, it is appropriate to conclude that electrometric techniques should not be relied on to give valid results in all situations. Additionally, it is not generally possible to determine the validity of a measured value without supplementary information. Therefore, electrometric methods would also appear to be most useful when used in conjunction with other methods.

2.3.2 Indirect Methods for Determining Eh

There are two indirect methods for determining the Eh of a geochemical system. The first involves straightforward calculation of the Eh based on thermodynamic principles. The second involves measuring the

concentrations of the ionic species in groundwater and then inferring the Eh from the relative concentrations of the ionic species in one or more redox couples.

2.3.2.1 Calculation of Eh

The calculation of Eh involves using a computer code to predict the mixture of ionic species present in ground water in equilibrium with a specified mineral assemblage. Knowledge of this information also allows the Eh and pH of the aqueous solution to be calculated directly using equations developed in Sect. 2.1.2.2.

There are two general classes of geochemical computer codes available today: ion-speciation/solubility codes and reaction-path-simulation codes, with the predponderance of the codes being in the ion-speciation/solubility class. There are many of these codes, the details of which have been both compiled and compared (Thomas, 1982 and Jenne, 1978). However, in the present instance, where the activity of interest is predicting the Eh of BWIP groundwater, the ion-speciation/solubility codes are not useful since they require the Eh (and pH) as input parameters rather than predicting them.

As a result, the applicable computer codes are the reaction-path-simulation class, with prominent examples being PHREEQE (Parkhurst, 1980) and EQ6 (Wolery, 1979). Briefly, these codes require temperature and the initial (unequilibrated) composition of the system as a

starting point. The code then begins to computationally allow the species initially present to react along a path leading to minimization of free energy. Results of the calculation are output at a number of pre-equilibrium steps as well as at equilibrium, when the calculation is finished.

Since the fundamental operation of the reaction-path-simulation codes depends on knowing the free energies of all existing and potential species of interest at the relevant temperatures and pressures, the thermodynamic data base employed in the calculation is critically important to the accuracy of the calculated results, including Eh. Unfortunately, thermodynamic data bases for this application are not adequate because (a) data for some important elements and compounds are absent or poorly known and (b) much of the data are available at temperatures and pressures much lower than those expected in repositories (Jenne, 1978 and Moody, 1982). Other problems with this class of codes include:

1. they do not include organic ligands in the calculations,
2. they assume that equilibrium is attained when, in fact, it may not be,
3. the reaction paths calculated may not be unique, depending on the system under consideration, and
4. the calculations do not include the time-dependency (kinetic) effects in the geochemical systems, and
5. the codes are unable to account for effects such as supersaturation.

Thus, the accuracy and validity of Eh values calculated with existing reaction-path-simulation codes would seem to be questionable unless the code had been verified or other, independent Eh measurements were available.

2.3.2.2 Inference of Eh

Another type of indirect method for determining Eh involves determining the activities of the members of several redox couples in the groundwater of interest. Stumm and Morgan (1981) point out that analytical determinations which are accurate within a factor of 2 will yield redox potential values within 5 to 20 mV depending on the number of electrons transferred in the process. Since the ratio of the members of certain redox couples (e.g., $\text{Fe}^{+2}/\text{Fe}^{+3}$, $\text{As}^{+3}/\text{As}^{+5}$) are very sensitive to Eh in the range of interest to BWIP, the measured ratios can be used to infer the relevant Eh. This method is subject to the usual limitations concerning being able to obtain unperturbed groundwater samples at the location of interest and being able to detect the species of interest at the generally low concentrations. An additional limitation of this method is that, while it may be one of the most straightforward ways to obtain an Eh value, it does not offer any promise of being able to extrapolate the result in either time or space for the perturbed repository.

The ion-speciation/solubility computer codes described in Sect.

2.3.2.1 can be employed with Eh as an independent variable to aid in the calculations required to match the measured compositions. This

type of exercise may be particularly useful if it can be shown that the groundwater species are at equilibrium and that the measured compositions agree well with the code predictions, thus providing some basis for extrapolation in time and space while verifying both the code and measurements.

2.3.3 Verification of Results

Based on the foregoing discussion, it is clear that all of the available and likely future methods for determining Eh values relevant to an unperturbed geologic repository and then being able to extrapolate it over time and space in the perturbed case are inadequate when used alone. The approach that will necessarily have to be employed is to measure/determine/calculate Eh using a variety of the techniques described herein. These values will then be compared to each other to determine if they reinforce/verify each other or, if not, why the discrepancies occur.

Finally, it is to be emphasized that the ultimate goal is the ability to predict Eh under post-closure repository scenarios. This will almost certainly require the use of the reaction-path-simulation geochemical computer codes, which will have to be validated using experimental data, presumably from the unperturbed repository. It will also require some validation of the assumption that the perturbed repository will approach some reasonable facsimile of the equilibrium condition predicted by the validated computer code in a reasonable amount of time, i.e., kinetic considerations must be addressed at some point in the process to validate the Eh values that will be applicable to determining input parameters for the performance assessment.

2.3.4 Summary of Methods for Determining Redox Conditions

Most of the parameters relevant to the determination of redox conditions, such as temperature, pH, ionic concentrations, etc., can be measured accurately using existing techniques. However, the central parameter in determining redox conditions, the redox potential (Eh) is more difficult to measure. The following methods have been used to measure Eh and have some potential applicability to a geologic repository:

1. colormetric indicators which change color at a specific Eh,
2. electrometric methods which involve using an electrode (typically platinum) to measure the potential,
3. calculation of the Eh using a reaction-path-simulation geochemical computer code based on the thermodynamic principal of minimizing the free energy of the system, and
4. inference of the Eh by measuring the relative amounts of the ionic species in various redox couples (e.g., $\text{Fe}^{+2}/\text{Fe}^{+3}$) and using the ratio to predict the Eh.

All of these techniques have limitations that are severe enough so that no single method can be relied on as giving the correct result. Therefore, the preferred approach is one of using multiple methods to determine Eh and comparing the results. If the results agree, this will be a powerful demonstration of methodological and parameter validity. If the results do not agree, the calculations or experiments will have to be reexamined for flaws or improper assumptions and repeated until agreement is attained.

3 SUMMARY AND CONCLUSIONS

Redox conditions represent the oxidation or redox potential (Eh), the redox stabilizing effect (poising) and the limiting rates of reactions in reestablishing equilibrium conditions.

In equilibrated systems, the redox potential (measured in volts) can be calculated from thermodynamic data and the activities of the reacting species by the Nernst equation. These redox potentials are the difference between the potential from the reacting species and the standard hydrogen electrode.

In aqueous systems, the Nernst equation also relates Eh to the pH that permit construction of Eh-pH diagrams, which are graphical representations (Eh as the ordinate and pH as the abscissa) that bound the regions of stability for the chemical species and possible solid phases. The complexities of natural systems and variations of Eh and pH with temperature and pressure prevent a complete characterization of the system by this means, but these diagrams are very useful in limiting the possible number of species and minerals that are effective in controlling geochemical behavior.

Construction of a repository will introduce perturbations in the geochemistry of the host rock and any subsequent mobilization of the waste package components will add complexity to the system. The kinetics of reestablishing equilibrium conditions are too complex for complete characterization, but bounding of the problem may be possible. The resistance to change of the redox potential (poising) is an important parameter in this respect. This resistance is measured in terms of the redox capacity; the higher the redox capacity, the greater the resistance to change. In iron-water systems, the redox capacity is greatest when

the activity of Fe^{3+} equals the activity of Fe^{2+} and the total iron concentration is high.

Redox reactions in natural systems are frequently irreversible and not at equilibrium. However, partial equilibrium may be approached in many cases and a metastable system may exist in which a working redox potential can be related to certain redox couples. In theory, it is possible to evaluate the redox potential in natural waters containing mixed couples by determining the relative activities of some (or all) members of the couples and then calculating the Eh for each couple with the Nernst equation. If the calculated Eh's for the couples are equal, the system is at equilibrium and the calculated Eh represents the system values. In practice, this is very difficult to accomplish.

The primary parameter in determining redox conditions, the redox potential (Eh) is difficult to measure. The following methods have been used to measure Eh and have some potential applicability to a geologic repository:

1. colorimetric indicators which change color at a specific Eh,
2. electrometric methods which involve using an electrode to measure the potential,
3. calculation of the Eh using a reaction-path-simulation geochemical computer code, and
4. inference of the Eh by measuring the relative amounts of the ionic species in various redox couples and using the ratio to predict the Eh.

All of these techniques have limitations that are severe enough so that no single method can be relied on as giving the correct result.

Therefore, the preferred approach is one that uses multiple methods to

determine Eh. If the results agree, this will be a powerful demonstration of methodological and parameter validity.

The ultimate goal is the ability to predict Eh under post-closure repository scenarios. This will almost certainly require the use of the reaction-path-simulation geochemical computer codes, which will have to be validated using experimental data. It will also require some validation of the assumption that the perturbed repository will approach some reasonable facsimile of the equilibrium condition predicted by the validated computer code in a reasonable amount of time, i.e., kinetic considerations must be addressed at some point in the process to validate the Eh values that will be applicable to determining input parameters for the performance assessment.

The following summarizes the information required by the NRC staff to assess the adequacy and acceptability of the proposed BWIP site characterization activities concerning redox conditions:

1. General approach - information concerning how redox condition data will be used in the characterization and licensing of the BWIP site.
2. Information to be acquired - information concerning redox conditions in the unperturbed repository, the redox capacity of the unperturbed repository, and redox conditions under which radionuclide migration might take place following repository closure.
3. Information acquisition plan - what types of data related to redox conditions will be acquired; what acquisition methods will be employed; what is the schedule and relationship of redox information acquisition activities?

4. Information verification - how will the information related to BWIP redox conditions be verified as being representative or bounding with respect to the actual situation in the post-closure repository?

4 REFERENCES

- Ames, L. L. and D. Rai, Radionuclide Interactions with Soil and Rock Media, EPA 520/6-78-007-A, U.S. Environmental Protection Agency, 1978.
- Baas Beeking, L. G. M., I. R. Kaplan, and O. Moore, "Limits of the Natural Environments in Terms of pH and Oxidation-Reduction Potentials," J. Geol., Vol. 68, p. 243, 1960.
- Benson, L. V., Secondary Minerals, Oxidation Potentials, Pressure and Temperature Gradients in the Pasco Basin of Washington State, RHO-BWI-C-34, Rockwell Hanford Operations, 1978.
- Bondietti, E. A., and C. W. Francis, "Geologic Migration Potentials of Technetium-99 and Neptunium-237," Science, Vol. 203, p. 1337, 1979.
- Carnahan, C. L. et al., Selected Hydrologic and Geochemical Issues in Site Characterization for Nuclear Waste Disposal: Flood Basalts at the Hanford Reservation, Draft Report, Lawrence Berkeley Laboratory, 1982.
- Eugster, H. P. and D. R. Wones, "Stability Relations of the Ferruginous Biotite, Annite," J. Petrology, Vol. 3, p. 82, 1962.
- Fairbridge, R. W., editor, The Encyclopedia of Geochemistry and Environmental Sciences, New York, Van Nostrand Reinhold Co., 1972.
- Garrels, R. M. and C. L. Christ, Solutions Minerals and Equilibria, New York, Harper and Row, 1965.
- Jenne, E. A., editor, Chemical Modeling, ACS Symposium Series 93, American Chemical Society, Washington, D.C., 1979.
- Krauskopf, K. B., Introduction to Geochemistry, New York, McGraw-Hill Book Co., 1967.
- Langmuir, D., "Eh-pH Determination," in Procedure in Sedimentary Petrology, R. E. Carver, editor, New York, Wiley Interscience, 1971.
- Latimer, W. M., Oxidation Potentials, Englewood Cliffs, N.J., Prentice-Hall, 1952.
- Moody, J. B., Radionuclide Migration/Retardation: Research and Development Technology Status Report, ONWI-321, Office of Nuclear Waste Isolation, 1982.
- Morris, J. C., and W. Stumm, "Redox Equilibria and Measurements of Potentials in the Aquatic Environment," in Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series, No. 67, American Chemical Society, 1967.
- Nightingale, E. R., Jr., "Poised Oxidation-Reduction Systems," Analytical Chemistry, Vol. 30, p. 267, 1958.

- Parkhurst, D. C., D. C. Thorstenson, and L. N. Plummer, "PHREEQE - A Computer Program for Geochemical Calculations," U.S. Geological Survey, Water Resources Investigations, 1980.
- Pourbaix, M. J., Thermodynamics of Dilute Aqueous Solutions, London, Edward Arnold Co., 1949.
- Rai, D. and R. J. Serne, Solid Phases and Solution Species of Different Elements in Geologic Environments, PNL-2651, Pacific Northwest Laboratory, Richland, Washington, 1978.
- Robie, R. A., B. S. Hemingway, and J. R. Fisher, "Thermodynamic Properties of Minerals and Related Substances at 298.15K and 1 Bar and at Higher Temperatures," Geol. Soc. Am. Bull., No. 1452, 1978.
- Rockwell Hanford Operations, Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3, 1982.
- Rydberg, J., Groundwater Chemistry of a Nuclear Waste Repository in Granite Bedrock, UCRL-53155, Lawrence Livermore Laboratory, 1981.
- Serne, R. J. and J. F. Relyea, The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program, PNL-3997, Pacific Northwest Laboratory, 1982.
- Sillen, L. G., "Master Variables and Activity Scales," in Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series, No. 67, American Chemical Society, 1967.
- Smith, M. J., et al., Engineered Barrier Development for a Nuclear Waste Repository Located in Basalt: An Integration of Current Knowledge, RHO-BWI-ST-7, Rockwell Hanford Operations, 1980.
- Stumm, W., "Redox Potential as an Environmental Parameter, Conceptual Significance and Operational Limitations," Third International Conference on Water Pollution Research, Section 1, No. 13, Water Pollution Control Federation, Washington, D.C., 1966.
- Stumm, W. and J. J. Morgan, Aquatic Chemistry, 2nd ed., New York, John Wiley & Sons, 1981.
- Thomas, S. D., B. Ross, and J. W. Mercer, A Summary of Repository Siting Models, NUREG/CR-2782, U.S. Nuclear Regulatory Commission, 1982.
- Thorstenson, D. C. and D. W. Fisher, "The Geochemistry of the Fox Hills-Bosal Hill Creek Aquifer in Southwestern North Dakota and Northwestern South Dakota," Water Resources Research, Vol. 15, No. 6, p. 1479, 1979.
- Whitfield, M., "The Electrochemical Characteristics of Natural Redox Cells," Limnol. Oceanogr., Vol. 17, p. 383, 1972.

Watanabe, N. and M. A. V. Devanathan, "Reversible Oxygen Electrodes,"
J. Electrochemical Soc., Vol. 111, p. 615, 1964.

Wolery, T. J., Calculation of Chemical Equilibrium Between Aqueous
Solution and Minerals: The EQ3/6 Software Package, UCRL-52658,
Lawrence Livermore Laboratory, 1979.

Zobell, C. E., "Studies on Redox Potential of Marine Sediments,"
Bull. Am. Petrol. Geologists, Vol. 30, p. 477, 1946.

APPENDIX T

~~TECHNICAL REPORT~~ CHARACTERIZATION OF RADIONUCLIDE SORPTION ON GEOLOGIC MEDIA

ABSTRACT

Sorption on geologic media can be an important repository aspect which retards radionuclide migration from high-level radioactive waste contained in stable geologic repositories to the accessible environment. Radionuclide sorption results from a number of geochemical processes and quantification of the sorption behavior and resulting migration retardation is desirable for repository performance assessment modeling. The geochemical processes responsible for radionuclide sorption by the engineered barrier constituents in the repository near-field and the host rock minerals or phases in the repository far-field are discussed. Experimental and generic thermodynamic methods for measuring or determining sorption values are reviewed and methods of data treatment and presentation as distribution coefficients or sorption isotherms are discussed. Uncertainties and difficulties encountered in extrapolating short-time small-size laboratory experimental results for the prediction of geologic-size and geologic-time repository behavior are described. Methods for determining sorption values and data analysis methods are presented. The radionuclide sorption information for the Basalt Waste Isolation Project Site is discussed, and needed future work is identified.

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1 INTRODUCTION

1.1 Background

1.1.1 DOE High-Level Waste Repository Program

The Department of Energy (DOE) High-Level Waste Repository Program is developing safe repositories for high-level radioactive waste and spent fuel from civilian nuclear power reactor activities. The program approach is to use confinement in stable geologic formations to insure that no environmentally deleterious or regulatorily unacceptable radioactivity releases to the accessible environment can be expected to occur after waste emplacement in the repository.

1.1.2 Repository Containment Goal

The goal of the high level waste repository program is to develop a repository in a stable geologic formation such that any credible release of radioactivity after waste emplacement would not exceed accepted and required standards. This has led the program to consider and evaluate three candidate sites: a large basalt flow at the Hanford Reservation, extensive tuff deposits at the Nevada Test Site, and an as-yet undesignated site(s) in a domal or bedded salt deposit. The near-term programmatic goal is to characterize these candidate sites with respect to applicability as a repository and to select one for licensing and operation.

1.1.3 NRC Approach to Radionuclide Containment

The NRC approach to radionuclide containment and isolation from the accessible environment is to define the credible events which could lead to or cause radionuclide migration and to assure that multiple barriers exist which would control or restrict migration to acceptable or required levels under any credible scenario. Radionuclide transport by groundwater intrusion and subsequent migration through the host rock formation is the most probable mechanism which could lead to release to the environment. Thus, great emphasis is placed on: (1) geologic and hydrologic aspects of the candidate sites which will restrict groundwater availability and the potential for groundwater movement through the

emplaced waste, and (2) to geochemical retardation processes or conditions which would limit or control radionuclide migration following groundwater intrusion. Evaluation and quantification of these two aspects of the candidate repository site are important NRC activities in developing the necessary background information to guide the NRC actions in permitting or disallowing DOE repository site development and operation.

Since exact establishment of expected future behavior in a geologic deposit over long times may be difficult to precisely quantify, the bounding approach to migration parameter bracketing may be pursued. With this approach, if it can be shown with certainty that the value of some process parameter cannot exceed some limiting value or boundary which satisfies the requirements, then determination of the exact value becomes less important and lack of determination of the exact value will not restrict the validity or usefulness of the bounding data. Such a bounding philosophy is useful and sometimes necessary when dealing with complex geological systems where precise geochemical data development may not be simple or even attainable.

1.1.4 Radionuclide Retardation

1.1.4.1 Retardation Processes and Conditions -

Multiple barriers will be employed to retard the migration of radionuclides from the emplaced waste to the environment via groundwater migration. These include: geologic isolation from groundwater, waste emplacement in an insoluble form, design of an engineered barrier to restrict groundwater contact with the waste, limited radionuclide solubility in repository groundwater, and sorption of solubilized radionuclides by the repository host rock. Important geochemical processes and conditions involved in the performance of these barriers include radionuclide dissolution, solubility, and sorption. This Appendix is directed toward the sorption process.

1.1.4.2 Application of Retardation Data -

Experimentally obtained or calculated values quantifying the geochemical processes and conditions responsible for controlling radionuclide retardation are

utilized in geochemical modeling of radionuclide migration and in performance assessment modeling of repository behavior. Such modeling activities form the basis for evaluation of the candidate repository sites and justification for licensing site activities.

1.1.5 Importance Of Radionuclide Sorption

Radionuclide sorption by the backfill and the host rock primary, secondary and accessory minerals and phases may be a major constraint to radionuclide migration in groundwater and is an important aspect of the redundant migration barriers. Therefore, it is an important and significant part of the NRC geochemical assessment of potential site performance.

1.2 Government Regulatory Framework

1.2.1 Role of U.S. Agencies

1.2.1.1 DOE -

The DOE is responsible for the technical research and development necessary to identify a safe repository site and for construction and operation of the repository after approval by the NRC.

1.2.1.2 NRC -

The NRC is responsible for reviewing and approving the DOE repository site development and issuing the appropriate construction and operating licenses consistent with regulations governing high level radioactive waste repositories.

1.2.1.3 EPA -

The EPA is responsible for the protection of the environment, including protection from radioactivity releases, and for the issuance of suitable regulations and requirements.

1.2.2 Relevant Sections of Draft NRC Technical Criteria (10 CFR 60)

Support E - Technical Criteria

60.111 Performance Objectives

- (b) Performance of the geologic repository after permanent closure
 - (1) overall system performance
 - (2) (11) control of releases
 - (3) (11) isolation period

60.122 Favorable Conditions

- (g) Geochemical conditions that
 - (1) promote precipitation or sorption of radionuclides

60.123 Potentially Adverse Conditions

- (b) Adverse conditions in the disturbed zone
 - (15) processes that would reduce sorption

Support F - Performance Confirmation

60.140 General Requirements

- (c) The program will include in-situ monitoring, laboratory and field testing
- (d) The confirmation program shall be implemented so that
 - (2) it provides baseline information and analysis of that information on those parameters and natural processes pertaining to the geologic setting

2 DISCUSSION

2.1 Sorption Issue

2.1.1 Definition of Radionuclide Sorption Issue

The goal of isolating high-level radioactive waste in a repository is to limit the migration of radionuclides from the emplaced waste to the accessible environment to levels low enough to comply with applicable regulations (e.g.,

10 CFR 60, 40 CFR 191, etc.). Implicit in such a goal is the scientific philosophy that while absolute assurance of zero migration to the environment within geologic times may not be demonstrable or attainable, it is possible to achieve high assurance and reliability of restriction of radionuclide migration to very low and acceptable levels. The approach of employing multiple redundant migration barriers will be utilized to insure satisfactory site performance. These barriers, given in sequence of their control of radionuclide migration, include: the waste form, the waste package, isolation by the repository from groundwater intrusion, the engineered barrier, low radionuclide solubility in groundwater, and radionuclide sorption on host rock primary, secondary and accessory minerals. Thus, radionuclide sorption is an important migration barrier and measurement, analysis, and utilization of sorption values in site performance modeling are be important aspects of site characterization and analysis.

2.1.2 Sorption Processes

2.1.2.1 Definition of Terms -

The term "sorption" as used in this Appendix covers or encompasses physical and chemical processes which can result in the removal of a solute from solution by interaction with a solid material or adsorbent.

As a result, it is necessary to indicate: (1) the type of sorption-related information that would be needed to support any sorption retardation arguments used in the repository licensing and (2) the acceptable approaches for obtaining this information. The generic term "sorption" is generally to be preferred in the discussion of solute removal by geologic materials such as rocks or soils because multiple processes often are involved, and the specific process or processes responsible for the removal may be either unknown or unquantifiable. Important sorption processes are discussed in the following sections. The sorption data is usually calculated and utilized as effective distribution coefficients (see Section 2.1.3) or sorption isotherms (see Section 2.3.6).

2.1.2.2 Ion Exchange -

Ion exchange reactions are often major contributors to mechanisms responsible

for radionuclide sorption by rocks or soils. In this process, charged sites on the surface of the adsorbent hold bound ions by electrostatic and/or van der Waals forces. The number of sites is limited and the ratio of solute molecules to the number of sites available affects the sorption value. Mass action competition between ions plays an important role in ion exchange sorption and radionuclide sorption by ion exchange is dependent upon the solution composition. Ion exchange reactions are usually relatively rapid and reach steady state or equilibrium in short times, thus the sorption and desorption rates or distribution coefficients should be equivalent for this process. Sorption data which shows wide differences between sorption and desorption should not be considered as resulting from simple ion exchange reactions. Ion exchange sorption values or distribution coefficients often display Langmuir isotherm forms since ion exchange in some cases may be considered as a single adsorbed layer at low concentrations on the adsorbent (see Section 2.3.6).

2.1.2.3 Surface Sorption or Chemisorption -

Chemisorption involves chemical interaction between the solute and the adsorbent and frequently is characterized by irreversible sorption. Surface sorption is essentially similar, except that the term is broader and can include any type of sorption process or processes (often of unknown nature and number) which lead to strong and difficultly reversible or irreversible surface sorption. Chemical change of the adsorbed solute on the surface of the adsorbent can result from redox reactions with adsorbent constituents, local pH changes, or other chemical reactions. Irreversible sorption behavior is frequently exhibited by radionuclides on rocks and soils, and with such chemically complex systems the actual chemical reaction(s) responsible may be difficult to determine. This has important consequences for batch distribution coefficient measurements (see Section 2.3.2.1) since values obtained on sorption will be lower than those obtained on desorption. Since the highest distribution coefficient will dominate the migration rate calculations, it is usually desirable to test all experimental systems for irreversibility by measuring desorption as well as sorption values. Chemisorption behavior often may be more representative of natural systems than ion exchange behavior and should always be considered as potentially dominating radionuclide sorption studies of geologic media.

2.1.2.4 Hydrolysis Precipitation -

Hydrolysis precipitation may be encountered in sorption experiments when the solution pH changes during the experiment to conditions such that solute solubility limits are exceeded. Under such conditions, solute precipitation will occur. The non-specific adhesion or inclusion of precipitate with the test solid adsorbent will lead to erroneously high sorption values or effective distribution coefficients. Sorption tests involving geologic materials are sometimes subject to radionuclide hydrolysis precipitation since reactions of soil or rock primary or secondary minerals with the test solution components can lead to increased solution pH's and decreased radionuclide solubility. This is particularly true for adsorbent materials which may contain dolomite or calcite, common basic minerals. Avoidance of hydrolysis precipitation during sorption laboratory test is one aspect of the necessity of maintaining the solute concentration below the saturated solubility limit during sorption measurements; without attention to this experimental limit, invalid and erroneously high sorption values or distribution coefficients may be obtained.

2.1.2.5 Coprecipitation -

If major solution components, such as silica, precipitate during the radionuclide sorption test, they may include trace constituents in the precipitate either by surface sorption or by lattice substitution phenomena. Thus, as with hydrolysis precipitation, solute or radionuclide atoms will be included in an additional new solid phase and erroneously high sorption values or distribution coefficients may be obtained. Coprecipitation is an ever present uncertainty in sorption tests with soils or rocks and can be difficult to detect physically in the laboratory test or after analysis of the resultant data.

2.1.2.6 Redox/Complex Speciation Alteration -

In conducting sorption tests, it is highly desirable to identify the species of solute or radionuclide being adsorbed. Otherwise, the sorption values obtained cannot be readily related to the system geochemistry, and the values could be subject to misinterpretation. This is a particularly vexing problem with

radionuclide sorption on rocks and soils since many fission products, and especially actinides, have multiple valence states and can form complex ions or polymers which may be stable under repository groundwater conditions. Recent work with plutonium (Cleveland, 1982) has shown that three valence states and at least two complex forms can simultaneously exist in some laboratory test solutions. It would be extremely difficult to differentiate the contribution of each of these forms to a sorption value or distribution coefficient obtained with such a test solution. As with coprecipitation, this is an ever present potential complexity that is not easily identified or resolved.

2.1.3 Distribution Coefficient

2.1.3.1 Definition of Terms -

Sorption values are frequently calculated as an empirical parameter, an effective distribution coefficient. This is simply the ratio of the concentration of the solute in the contacted test solid adsorbent to the concentration of the solute on the contacted test solution. In the case of radionuclides at low concentrations, the actual concentration often is not determined and the distribution coefficient is calculated from the corresponding counts per minute or disintegrations per minute data. Since volume is being divided by mass in calculating the distribution coefficient, the units are liters per kilogram (L/kg) or milliliters per gram (mL/g). In the past, there has been no generally accepted standard symbol to represent the distribution coefficient and various symbols were used. Recently, standard symbols and terminology have been recommended (Serne and Relyea, 1982). "Kd" should be reserved for distribution coefficients which have been obtained under equilibrium conditions. Few experiments can be rigorously demonstrated as being at true equilibrium; thus, most experimentally-derived distribution coefficients should be represented by the symbol "Rd", which is the effective distribution coefficient and is simply the measured ratio of concentrations for some test and does not imply equilibrium or reversible conditions. The symbol "D" should be reserved for distribution coefficients which have been calculated from thermodynamic routines. This recommendation does not seem to have found general acceptance, and most authors continue to use Kd or K_d for both effective and equilibrium distribution coefficients.

2.1.3.2 Techniques for Measuring Distribution Coefficients -

Effective distribution coefficients are measured in laboratory tests that involve contacting the solute or radionuclide in a solution with the solid adsorbent. Various mechanical means of achieving this have been utilized; each has advantages and disadvantages (see Section 2.3).

2.1.3.3 Analytical Methods and Limitations -

Alpha and gamma radioactivity counting techniques are usually employed for the measurement of radionuclide concentrations. These are much more sensitive than most conventional chemical analytical methods; but even so, measurement of very low concentrations of actinides (alpha emitters) or of some fission products with weak gammas can be difficult. A further complication is the poor capability of alpha detection techniques to distinguish between very close alpha energies; thus, measurement of several actinides at once can become complex. With proper attention to experimental design and selection of the test radionuclide, however, these limitations can normally be circumvented and very sensitive and accurate radionuclide concentration analyses can be obtained which, in turn, yield sensitive and accurate distribution coefficient values.

2.1.3.4 Equilibrium vs Non-Equilibrium Conditions -

Attainment of equilibrium conditions during sorption tests is desirable. Many chemical reactions with geological materials may be slow, relative to the experimental test time, and often equilibrium or steady state is not attained. Under non-equilibrium conditions, the measured sorption value becomes dependent upon the test time, and data comparison and analysis becomes more complex and uncertain.

2.1.3.5 Reversible vs Irreversible Conditions -

If equilibrium conditions have been established in the sorption experiments, then both sorption and desorption techniques yield the same radionuclide distribution coefficient. Equilibrium and reversibility often are not attained,

however, and desorption often yields substantially higher distribution coefficients than sorption. Chemisorption reactions frequently lead to irreversible conditions (see Section 2.1.2.3).

2.1.3.6 Sorption Data Application -

Single distribution coefficient values are frequently used to represent radionuclide sorption behavior in retardation calculations. This is rigorously valid only if the distribution coefficient value meets all the following conditions: (1) the distribution coefficient is independent of radionuclide concentrations, (2) only a single solution species of radionuclide is present in the test, and (3) thermodynamic equilibrium has been attained in the test, i.e., sorption and desorption are equivalent. These three requirements are seldom met in complex geologic systems. Sorption isotherms (see Section 2.3.6) may be utilized to accommodate distribution coefficients which are dependent upon radionuclide concentration, although this makes calculation of radionuclide retardation more complex. Column chromatographic methods may be used to test for multiple speciation effects (see Section 2.3.2.2). Also, batch sorption/desorption tests may be employed to evaluate reversibility (see Section 2.1.3.4).

2.1.4 Relevance/Uncertainties/Difficulties of Extrapolating Laboratory Sorption Measurements to Repository Behavior Over Geologic Times

2.1.4.1 Groundwater/Rock Ratios -

In the repository, the host rock volume to groundwater volume is very large and rock mineral chemical and sorption reactions tend to dominate the radionuclide sorption processes. In the laboratory sorption tests, however, practical considerations require that the groundwater volume be greater than the rock or adsorbent volume, otherwise liquid samples may not be attainable for analysis after the test. Thus, chemical and sorption reactions which are mass-action controlled, such as ion exchange, may lead to quite different distribution coefficients in the laboratory test and in the repository. Such potential differences need to be carefully considered when extrapolating laboratory results for predictions of repository behavior.

2.1.4.2 Reactions of Primary, Secondary and Accessory Minerals and Amorphous Phases -

The sorption values measured in laboratory tests or attained in the repository are highly dependent upon the solid adsorbent phases involved. In laboratory tests, crushed whole rock samples may expose principally primary mineral surfaces to the test groundwater, while groundwater migrating through a repository would experience a much greater exposure to aged primary mineral surfaces and to the secondary and accessory minerals which are concentrated in the rock fissures and permeable zones. Thus, radionuclide distribution coefficients obtained in laboratory tests could be quite different from those experienced with migrating groundwater in the repository. Non-crystalline or amorphous phases may also be present in the repository host rock and the mineral/amorphous phase ratio of solids in laboratory tests and in repository conditions may also be different and contribute to uncertainties and difficulties in data extrapolation to expected repository behavior.

2.1.4.3 Reaction Kinetics Limitations on Time Extrapolation -

The differences in time scales for laboratory tests (hours, days, or months) and repository operation (thousands of years) is a major source of uncertainty in predicting repository performance. Many geochemical reactions in heterogeneous media can be very slow; for example, silica dissolution and reprecipitation, radionuclide solid recrystallization, etc., and laboratory tests may not reach or even approach equilibrium or steady-state conditions. Extrapolation of the experimentally-obtained distribution coefficient to repository times may introduce substantial uncertainties and difficulties. Definition or understanding of valid time-extrapolating techniques may be one of the more significant problems and uncertainties faced by performance assessment modeling.

2.1.4.4 Radionuclide Speciation Alteration Effects -

The radionuclide distribution coefficients are highly dependent upon the radionuclide solution speciation. Thus, in designing sorption experiments, it is desirable to add the radionuclide to the groundwater in the correct or equilibrium chemical species, if possible. Changes in speciation may be slow,

however, and can introduce uncertainties. Since the radionuclide concentrations in groundwater are very low, complex formation or redox reactions with groundwater major, minor, or trace constituents or with host rock minerals must always be considered a complicating possibility.

2.1.4.5 Groundwater/Host Rock Reactions -

Both rapid and slow geochemical reactions may occur between the groundwater and geologic adsorbent during the sorption test. Slow reactions can lead to non-equilibrium conditions and complicate data extrapolation. Since the groundwater/rock ratio will be different in the laboratory test than in the repository test conditions, measured distribution coefficients may not be exactly representative of repository radionuclide sorption behavior.

2.1.4.6 Thermal and Radiation Pulse Effects -

The thermal pulse from the waste canister can profoundly alter the chemical and physical properties of the groundwater, backfill, and host rock in the near-field environment. Laboratory tests designed to measure radionuclide sorption behavior in the near-field, or with altered groundwater that has passed through the near-field, must take these changes into consideration. Minerals may dehydrate or recrystallize and both major and minor groundwater constituents may be increased or precipitated. Silica may dissolve and then reprecipitate. Radiolysis of the water may form hydrogen peroxide and O_2 and H_2 gases which are chemically reactive and may alter radionuclide speciation. Such complex potential behavior must be considered in designing and interpreting sorption tests.

2.2 Information Needs

2.2.1 General Goals

2.2.1.1 Radionuclide Containment -

The goal of the repository operation is to confine emplaced high-level radioactive waste in a manner that complies with applicable regulations. To determine compliance, sufficient information is needed to describe predicted repository

behavior under credible release scenarios. With respect to sorption on geologic media, this requires knowledge of the sorption values or distribution coefficients for all the key radionuclides under geochemical conditions to be encountered under release scenarios.

2.2.1.2 Data Sufficiency, Accuracy, and Defensibility -

The sorption data used in repository performance assessment modeling to predict radionuclide release values must meet tests of sufficiency, to assure that all the needed information is available, and accuracy, to establish values with acceptable precision and defensibility to withstand the scrutiny of the licensing process.

2.2.2 Bounding Approach

2.2.2.1 Resolution of Sorption Issue -

The bounding approach to parameter bracketing may be followed since exact future behavior in a geologic repository over long times may be difficult to precisely quantify. In this approach, sufficient, accurate and defensible sorption values or distribution coefficients are essential only to bound or limit the actual value since the measurement of the precise value may be experimentally complex and difficult, or even unattainable. If it can be shown that the value is within some bounding limit, this would be sufficient; determination of the precise value, while still desirable, would not be mandatory. This approach to sorption experimental design and execution may substantially simplify the experimental needs.

2.2.2.2 Expected vs Worst Case Behavior -

Two classes of release scenarios may be considered in modeling credible radionuclide release from a repository. These are expected behavior and worst case behavior. Analysis of the expected behavior case requires precise and accurate input data. Thus, modeling expected radionuclide sorption behavior would require knowledge of the exact values of the distribution coefficients. Under the bounding approach, however, it may be possible or necessary to

restrict modeling considerations to worst case behavior. The bounding approach allows consideration of limits, and if the limiting sorption values or distribution coefficients show acceptable worst case radionuclide release, then additional experimental work to exactly define the distribution coefficients for expected behavior may not be necessary.

2.2.3 Data Acquisition Plan

2.2.3.1 Identification of Key Minerals and Phases -

Measurement of sorption values or distribution coefficients and sorption isotherms involves contacting groundwater and solid adsorbent materials. Great care must be exercised in selecting the solid adsorbent to assure measurement of valid and meaningful values. Site specific backfill or host rock materials must be used. These can be quite complex, however, and composed of primary, secondary, and accessory minerals as well as amorphous or glassy phases. Each of these minerals and phases can display different distribution coefficients for each radionuclide; therefore, the test solid adsorbent sample should be selected so as to be representative of the repository situation under investigation. Determination of distribution coefficients requires considerable prior knowledge of the backfill and host rock mineralogy and geology. Certain mineral or glass phases likely will play key roles in establishing radionuclide sorption behavior, and identification of these and concentration of the sorption experimental work on these key phases can help minimize the experimental effort.

2.2.3.2 Characterization of In-Situ and of Thermal-Pulse/Post-Breach Altered Groundwater -

Measurement of sorption values involves contacting groundwater and solid adsorbent materials. As for the adsorbent (see Section 2.2.3.1), great care must be exercised in selecting the groundwater sample to be used in the test. The radionuclide sorption values or distribution coefficients are highly dependent upon the groundwater chemical composition: pH, Eh, and major and minor ionic and colloidal constituents. In-situ groundwater may be considerably altered by the chemical and physical events associated with the thermal pulse and canister

breach conditions; thus, the migrating groundwater containing the released radionuclides may be quite different from the in-situ groundwater. Attention should be directed toward understanding groundwater alteration reactions and to determination of sorption values from altered groundwater. Reprecipitation of groundwater constituents may also occur in altered groundwater, and formation of colloidal solids must be evaluated. An understanding of these sorption parameters should be developed in order to obtain valid and defensible sorption values.

2.2.3.3 Identification of Key Radionuclides -

In establishing repository performance and safety, certain radionuclides will likely dominate the release calculations and environmental considerations. Identification of these key radionuclides early in the experimental program and restriction of the bulk of the sorption experimental effort to these key radionuclides will simplify the laboratory work necessary. Continued interaction between the laboratory effort and the performance assessment activities is highly desirable and would aid in the selection and identification of the key radionuclides.

2.2.3.4 Establishment of Bounding Radionuclide Migration Conditions -

Employment of the bounding approach to radionuclide migration (see Section 2.2.2) will help select and restrict the experimental effort involved in developing sorption values. Thus, under this developmental philosophy, only certain limiting radionuclide migration cases need to be quantified and other, non-limiting cases or parameters become of secondary importance.

2.2.3.5 Laboratory Measurement of Key Radionuclide Sorption Values or Distribution Coefficients -

After consideration of the key groundwater/adsorbent/radionuclide/ parameter conditions (see Sections 2.2.3.1 through 2.2.3.4), the data acquisition plan then should specify the laboratory sorption measurements required. (The laboratory methods available are discussed in Section 2.3.) The data acquisition plan

should delineate a logical sequential plan for obtaining the needed sorption values in consort with their application in repository performance modeling.

2.2.3.6 Field Validation of Laboratory Measurements -

Extrapolation of small-scale short-time laboratory measurements to expected behavior in geologic formations over long times can be complex (see Section 2.1.4). Therefore, the data acquisition plan should include limited, carefully designed field tests to validate key laboratory sorption values.

2.2.3.7 Data Compilation and Analysis -

Various methods have been used by different experimenters to relate distribution coefficient relationships to geochemical parameters (see Section 2.3.6). Attention should be given to the data format needed in migration modeling when establishing the data acquisition plan. This may be particularly important if various isotherms will be required or encountered (see Sections 2.3.6.2 through 2.3.6.4).

2.3 Methods for Determining Sorption Values

2.3.1 General

2.3.1.1 Empirical Laboratory Methods -

Sorption values, conventionally expressed as distribution coefficients (see Section 2.1.4.1), are frequently determined by empirical laboratory methods. These are empirical in the sense that no prior information or knowledge of the composition or properties of the adsorbent or the solution are required; they are used in the test and a sorption value measured. For these types of tests, samples of a solution containing the radionuclide(s) of interest and a solid adsorbent are contacted in small laboratory containers or apparatuses for limited periods of time. The solution and solid are then separated and the solution is usually analyzed to measure the radionuclide concentration and the sorption of the radionuclide onto the solid is calculated. The solution and solid can be pure chemical components, synthetic groundwater and selected

characterized minerals, rocks or soils, or can be site-specific well water and rock samples. The interpretation of the sorption values or distribution coefficients obtained can be complex, however, as discussed below (see Section 2.3.3), and extrapolation of empirical data from small laboratory tests to the prediction of radionuclide behavior in a repository over geologically significant times may be uncertain. This stems, in part, from the fact that the empirically determined sorption values can result from the combination of effects of several simultaneous sorption processes (see Section 2.1.3) and the contributions of each to the sorption value obtained usually are unknown; thus, the values cannot easily be extrapolated to other conditions with precision or confidence. Notwithstanding these constraints, empirical laboratory methods have been used by many laboratories for years, and a large body of published sorption values or distribution coefficients exists.

2.3.1.2 Mechanistic/Generic Thermodynamic Methods -

Recently, some scientific effort has been directed toward the development of computer codes or models which are capable of calculating sorption values from fundamental knowledge of the system components (solution and solid phases) and their behavior derived from thermodynamic principles. Such calculations are advantageous, since they can be performed with mathematical rigor and can be extrapolated to cover any parameter(s) of interest or application to the repository. A considerable body of fundamental thermodynamic and geochemical information must be known, however, in order to support the calculational codes. The current incomplete state of the supporting data bases, especially for actinide elements, is a major limitation for this method of obtaining sorption values applicable to waste repository sites. The research community is directing considerable attention to these data base needs and the usefulness and validity of the mechanistic/generic thermodynamic methods should improve in the future.

2.3.2 Description of Laboratory Methods

2.3.2.1 Batch Tests -

Batch tests are inherently easy to carry out in the laboratory. Many investigators have chosen this method and a large body of sorption values exist in the

literature which were obtained by batch test methods. A batch test consists of contacting the adsorbent with a solution containing the radionuclide(s) of interest in a container. Usually a small glass or plastic bottle is employed as the test container. The container always is agitated by some method, usually by mechanically shaking or rotating the container for the duration of the test period. In some cases, larger samples may be contacted in a stirred test vessel. The container atmosphere usually is air but may be nitrogen or other gas mixtures to simulate anoxic conditions. Frequently the test is conducted at ambient temperature in the laboratory, or for greater precision in the temperature control or to conduct tests at elevated temperatures, the test container may be placed in a water or air thermostat. The test contact time may vary from a few minutes to days or even months. Normally the tests are carried to constant or steady state sorption values. For some geologic materials this has required extended contact times. After the desired contact time, the adsorbent and solution are separated, usually by centrifugation or filtration. Usually the alpha or gamma emitting activity of the test solution prior to the test and after contact with the adsorbent are determined by appropriate radionuclide counting techniques, and these count per minute numbers are used to calculate the sorption value or distribution coefficient (see Section 2.1.4.1). Despite the ease, simplicity, and concomitant low cost of batch sorption tests, great care must be exercised in selecting the test solution and adsorbent and the laboratory test parameters. Even with attention to these aspects, interpretation and application of batch sorption data is not always completely straightforward (see Section 2.3.3) and alternate experimental methods have been sought and evaluated (Serne and Relyea, 1982).

2.3.2.2 Once-Through-Flow Column with Intact or Disaggregated Adsorbent -

In this laboratory method the adsorbent, usually a soil or rock sample, is placed in a column and the test solution is allowed or caused to flow through the column. The objective of this test configuration is to attempt to more closely model the migration of solutions or groundwaters through a geologic member such as a soil layer or rock strata. The adsorbent may be either a solid continuous rock sample or may be a soil or rock crushed to a desired particle size. The test solution may be a pure chemical solution, a synthetic groundwater, or an actual well water sample. Flow through the column may be downflow by gravity

but more frequently is upflow in order to aid in displacing air from the column. For upflow, a mechanical pump or other pressure-generating device is used. The column temperature may be ambient or a jacketed column may be used and the temperature maintained at a constant value by circulating thermostated water through the jacket. The test time may be varied, dependent upon the flow rate established or attainable. For solid rock samples or fine soils, the very slow flow rates attainable may restrict the test parameters to only long times. The column effluent is collected and sampled, frequently by obtaining sequential samples with a mechanical fraction collector. The radionuclide concentration is usually determined by alpha or gamma counting techniques in the initial solution and in the effluent samples, and these concentrations or counts per minute numbers are used to calculate a series of sorption values or distribution coefficients as a function of time. This experimental method is considerably more complex than the batch test method and generally has been correspondingly less frequently employed. It has the advantage, however, of yielding time-dependent data and of more closely modeling the field conditions of groundwater migration in the repository in the laboratory tests.

2.3.2.3 Recirculating-Flow Column with Intact or Disaggregated Adsorbent -

The recirculating-flow column method is similar to the once-through-flow column method with the exception that the column effluent solution is recirculated through the column instead of being discharged and collected. The purpose of this is to attempt to overcome kinetic problems encountered in once-through tests where the adsorption rate is significantly slower than the solution residence time in the column. Under those conditions, equilibrium or steady state can never be achieved in a once-through column, and the measured sorption values will be lower than steady state values. By recirculating the solution containing the radionuclide, the effective contact time can be extended to any desired value. Usually the recirculating solution is sampled periodically and analyzed for radionuclide content and these numbers are used to calculate a series of sorption values as a function of time. The longer contact times attainable with the recirculating-flow laboratory column method may help to more accurately model the behavior of groundwater in a repository; however, the extended experimental times and increased experimental complexity involved have limited the application of this method.

2.3.2.4 Axial Filtration -

Axial filtration is an experimental technique developed to attempt to combine the advantages of both batch methods (rapid contact of all adsorbent particles) with column methods (development of loading and elution curves) (Triolo, Harrison, and Kraus, 1979). The method has not found widespread application, however, due to both theoretical and practical problems. Development of distribution coefficients is simple only for systems which display linear isotherms. The mathematical treatment can be quite complex in cases displaying curved isotherms, the most prevalent case for many geologic systems. Also, the experimental apparatus is more complex than that encountered in batch or column methods and more prone to leaks of radioactive solutions, etc. Axial filtration may not see significant application in the future.

2.3.2.5 Channel Chromatography -

Channel chromatography is a new method and has been considered [Francis, et al (1977)] as a technique for determining distribution coefficient values on geologic materials. The technique is similar to column methods except that the soil is placed in an open channel. The method does not appear to have found widespread acceptance.

2.3.3 Discussion of Laboratory Methods

2.3.3.1 Theoretical Development and Assumptions -

The empirical laboratory methods do not rest on a foundation of theoretical principles. They measure a sorption value or distribution coefficient obtained by contacting a solution and an adsorbent under some set of experimental parameters. This is both the strength and the weakness of this method. The strength is that it is simple and direct, while the weakness is that without any understanding of the underlying principles and processes, the values obtained cannot be extrapolated to other conditions or time frames. Because of the inherent complexity of and limited information about geologic processes and conditions, however, empirical methods are often the only methods available, and a great deal of sorption information has been developed by these methods.

2.3.3.2 Chemical and Physical Constraints -

Empirical laboratory methods of measuring sorption values or distribution coefficients can yield numbers applicable to large-size and long-time waste repository conditions only if the test parameters approximate those to be encountered in the repository. Thus, to obtain meaningful numbers, a considerable body of information about the expected repository parameters must be known and the laboratory test parameters must be correspondingly established. Depending on the application of the sorption values or distribution coefficients desired and the chemical and physical properties of the specific repository, parameters such as the following must be known for the repository and controlled in the laboratory: solution composition, both major and minor constituents; radionuclide concentration and speciation; pH and Eh; adsorbent selection, homogeneity or heterogeneity, particle size and surface area; time and temperature; speciation and solubility of the radionuclide; and solution/adsorbent reactions. Even with careful attention to these parameters, duplication of measured sorption values in various laboratories may not be totally straightforward (Relyea et al., 1980).

2.3.3.3 Redox Control

Geochemical experiments involving measurement of radionuclide solubility and/or sorption must be carried out under defined and reproducible redox conditions in order to collect meaningful, valid, and defensible data for utilization in radionuclide retardation modeling or assessment. Since the valence or oxidation state of any element is a function of both the system oxidizing-reducing potential (Eh) and acidity-basicity (pH), knowledge of the redox state requires definition of both pH and Eh. Without knowledge and control of the redox parameters, radionuclide speciation (both oxidation state and possible complex formation) will be unknown and may vary during tests in an irreproducible manner. Under such conditions, the sorption results can be meaningless and/or misleading. Various experimental techniques can be employed to set and control the solution pH and Eh. These include both internal, i.e., within the solution, and external experimental aspects.

Since the oxygen content of normal air is a relatively strong oxidant and has low but significant solubility in aqueous systems, all aqueous systems exposed to air would eventually result in the dissolved species being oxidized to their state in equilibrium with the experimental activity of dissolved oxygen. In many experiments, the kinetics of the reaction is often slow enough and the experimental time short enough that air oxidation does not introduce serious complications. However, for tests to measure geochemical properties or reactions of radionuclides present at trace concentrations in groundwater/mineral systems which are poorly poised and may require extended test times of weeks or months, air oxidation can become a very important experimental parameter. If measurement of sorption values under anoxic or reducing conditions is desired, then extensive experience by many investigators has shown that it is essential to exclude air from the test apparatus. Frequently, closed containers filled or flushed with an inert gas such as argon or nitrogen are employed. Recent experience (Meyer et al., in press) with strongly reducing and poorly poised systems, such as BWIP basalt-groundwater, has shown that even carefully constructed apparatuses frequently leak air and lead to erroneous results. In such cases, the only practical solution has been to enclose the entire test apparatus in an inert atmosphere glove box. Use of a glove box, while both cumbersome and expensive, is strongly recommended for Eh control with reducing geochemical systems. For tests involving significant amounts of alpha activity, use of an alpha containment glove box may be necessary for radiologic safety considerations and the addition of any inert glove box atmosphere then does not represent a major additional test complication.

The acidity-basicity (pH) of an aqueous system is not significantly affected by the test vessel atmosphere, except indirectly as a result of oxidation-reduction reactions. Thus, external controls are neither necessary or employed.

Two types of internal controls have been utilized to attempt to hold test solutions at a fixed and known Eh. These are: addition to the experimental solution of chemical couples which poise the system at a known Eh, and electrolytic methods of adjusting the valence or oxidation state of existing solution components through the use of a potentiostat and inert electrodes in the test solution.

The term "redox buffer" means pairs of reagents like Fe(II)-Fe(III) or Os(II)-Os(III) that can poise the potential of a solution to a value determined by the equilibrium potential of the pair. There are two fairly obvious difficulties with use of redox buffers that greatly limit their usefulness. First, any individual redox buffer will have a limited range of potentials of usefulness. The potential can be varied to some extent by changing the ratio of the oxidized and reduced forms or the pH, but in order to get a wide range of potentials and pH's, a number of buffers must be used. Perhaps the most serious difficulty is the possibility that the buffer introduces a new variable into the adsorption experiment, and therefore, it must be demonstrated that the presence of the buffer does not alter the characteristics of the adsorbent with respect to the particular sorption reaction under study. These same considerations apply to the use of single reagents like powerful redox reagents (hydrazine, ozone, etc.) which are sometimes used to insure that a radionuclide is in an upper or lower valence state. Again it must be demonstrated that they do not alter the mineral, or they must be removed prior to contact with the mineral. Similarly, the pH can readily be fixed at a given value through use of pairs of reagents (often phosphates) that determine the solution H^+ or OH^- activity. The use of pH buffers is well developed, i.e., for standardizing pH meters. As with Eh buffers, however, it is necessary to establish that complex formation between the buffer and the radionuclide species does not occur and that new insoluble compounds are not formed or that the buffer preferentially adsorbs on the mineral surfaces or reacts with the mineral. Without adequate consideration of such concerns, the validity of the sorption data may be compromised.

Detailed descriptions of apparatus and methods for studying redox reactions relevant to sorption measurements have been described by the author and co-workers (Meyer et al., in press). The electrolytic method of controlling valence state is a particularly convenient method. It incorporates a porous electrode into a circulating column apparatus for measuring sorption ratios. The high surface area of the porous electrode makes its use especially efficient in carrying out valence change reactions. The main advantages of the electrolytic method of controlling valence state are that no chemical reagents need to be added to the solution and the electrode potential can be controlled to any desired value by using a potentiostat. Disadvantages are that the radionuclide can adsorb on the electrode, and that if the potential is in the range of hydro-

gen or oxygen evolution, reactions will occur that will slowly change the pH. This change of pH is particularly troublesome at neutral solutions which are unbuffered since only a small amount of acid or base can significantly alter the pH.

2.3.3.4 Previous Applications -

Empirical laboratory methods for the determination of sorption values or distribution coefficients have been extensively employed in the past for high-level waste repositories as well as many types of radionuclide or hazardous material sites. Such measurements are also frequently applied to geochemical studies of ore formation, solution leaching, mineral formation or alteration, soil chemistry, etc.; thus, the laboratory techniques and data analysis methods have been extensively investigated. The DOE laboratories have devoted attention to the sorption behavior of radionuclides at candidate waste repositories, and a substantial body of sorption values or distribution coefficients exist for the basalt, tuff, and salt candidate repository sites [Ames and McGarrah (1980); Daniels and Wolfsburg, 1981; Dosch, 1980; Erdal, 1979; Erdal, 1980; Erdal, et al., 1978; Francis and Bondietti, 1979; Lynch and Dosch, 1980; Moody (1981); Rouston, Barney, and Smith, 1981; Salter, Ames, and McGarrah, 1981a; Salter, Ames, and McGarrah, 1981b; Serne and Relyea, 1982; Serne, Rai, and Relyea, 1979; Vine, et al. 1981a; Vine et al. (1981b)].

2.3.3.5 Limitations and Uncertainties -

As with any experimental method, certain limitations and uncertainties are encountered which affect the precision and accuracy of the values obtained in laboratory tests and thus the reliability and defensibility of radionuclide migration predictions or performance assessment calculations which employ these sorption data. Many factors may be considered, but a number are frequently important and these are briefly discussed. Since distribution coefficients are highly dependent upon the test parameters, it is essential that the test pH, Eh, solution composition and adsorbent solid be representative of the repository conditions being evaluated. Particular attention must be paid to the rock or soil specimen since sorption may be quite different on major, secondary, or accessory mineral phases. Severe analytical uncertainties may be encountered at

very low concentrations of radionuclides, and careful attention must be given to counting techniques and means of correcting for sorption by the container (blank correction), as well as differentiating between dissolved and dispersed radionuclides. Since the distribution coefficients are to be used in predicting radionuclide migration or repository behavior over very long times (1000s of years), it is desirable that the experiments be conducted so that steady state or equilibrium sorption values are obtained, if possible. Otherwise, extrapolation to long times may introduce serious errors. Radionuclide concentration often has a major effect on the measured distribution coefficient, and a more accurate model of sorption behavior can frequently be obtained from sorption isotherms constructed from values at different radionuclide concentrations than from single values (see Section 2.3.6). Differential experiments are often performed with one radionuclide at a time; however, since complex interactions can occur between radionuclides, such differential tests may not adequately describe their behavior. Integral tests involving a mixture of radionuclides may more realistically model repository behavior, but this approach is seldom used, due in part because of the analytical complexities introduced.

2.3.3.6 Anticipated Future Improvements -

Batch tests, supported by column tests, likely will remain the preferred laboratory test methods. As improvements are available in the counting instrumentation, this will allow extension of sorption measurements to lower radionuclide concentrations. The greatest near-future improvements probably lie in the areas of data analysis and presentation (see Section 2.3.6).

2.3.4 Description of Mechanistic/Generic Thermodynamic Methods

Several methods have been suggested for calculation of sorption behavior based on knowing certain parameters relative to the sorption reaction. If it can be shown that sorption in a particular system is an ideal ion exchange process, then ordinary ion-exchange equations can be used to calculate sorption behavior. In order to make this calculation, the sorption capacity of the solid sorbent and the equilibrium constant for the ion exchange reaction must be determined. Near ideal behavior has been observed for some systems, e.g., Sr^{2+} on clay minerals, (Rafferty et al. 1981), but for most systems of interest to waste

isolation, sorption does not generally obey these ideal ion exchange behavior. Other correlations have been observed for ion-exchange on sorbents like hydrous oxides which have variable sorption capacities, but the amount of data required to characterize even a single well-purified adsorbent sufficiently for sorption behavior to be calculable is quite large. An elaborate "site-binding" model has been developed (Davis et al. 1978) which combines a geochemical code with equations for sorption equilibria assuming surface complexation reactions with specific sites on the sorbent (site-binding). This model has been applied to sorption of Cs^+ and other ions on purified clays and oxides with fairly good agreement with experimental data (Silva et al. 1980).

2.3.5 Discussion of Mechanistic/Generic Thermodynamic Methods

Sorption reactions under repository conditions are enormously complicated. Speciation of all of the nuclides must be determined and adsorbing surfaces identified and characterized. Thus, the task of calculating sorption behavior from ion exchange, site-binding, or other models is an extremely difficult undertaking. However, use of these models can be useful for correlation of experimental data. It is possible that even for complex repository conditions, an approximation to typical ion exchange behavior might be observed for ions like Sr^{2+} and Ra^{2+} . Such a situation could occur if clays dominate the sorption behavior. If such is the case, then ion exchange theory would lend considerable confidence to the experimental data and to interpolation and extrapolation to untested conditions. Similar considerations apply to the more complicated site-binding and complex ion-exchange models.

2.3.6 Presentation of Data

2.3.6.1 Single Values -

Single distribution coefficient sorption values obtained for a given solution and adsorbent under a defined set of test parameters are frequently presented in data tables. Often, the tables consist of a comparison of various adsorbents under one set of fixed conditions, although any one test component or parameter could be systematically varied, depending on the test purpose. Such tables are useful for screening or gross comparison purposes, but have only limited use-

fulness for a more refined analysis since the single values give no hint of how they may vary with changes in test conditions. If more than one variable has been allowed to change in the tests used to obtain the distribution coefficient values, then comparison of the values may be of only limited validity, and such values ideally should not be combined in a single table.

The migration retardation of radionuclides dissolved in groundwater due to the sorption geochemical process is expressed as a retardation factor, R , which is related to the experimentally measured sorption distribution coefficient, K_d , by the relationship

$$R = 1 + K_d(\rho/\phi) ,$$

where

R = retardation factor (dimensionless)

K_d = distribution coefficient (mL/g)

ρ = geologic media bulk density (g/mL)

ϕ = geologic media porosity (dimensionless) .

This idealized expression is rigorously valid only when K_d is independent of radionuclide concentration and the sorption process is thermodynamically reversible. These conditions are not met in most practical applications and thus judgment must be exercised in the design of the distribution coefficient measurement experiments and in extrapolating the results of the small-scale laboratory experiments to predict geologic-scale behavior of radionuclides.

2.3.6.2 Empirical Isotherms -

It has long been recognized that the distribution coefficient is frequently a function of the solute concentration and plots of adsorbed concentration vs solution concentration have been employed as a method of presenting the data. Such plots have been called isotherms, although in practice, of course, all test parameters other than concentration must be held constant, not just the test temperature. Adsorbed species, including many radionuclides on soils or rocks, sometimes display a curved dependency of quantity adsorbed vs concentration similar to that classically observed for the sorption of gases on solids. Such behavior was initially described by Freundlich in 1907, and his name has become a generic label for any type of sorption plot showing such a curve. Similarly,

Langmuir in 1926 developed an adsorption isotherm for gases on solids based on the assumption of a unimolecular surface and, for ideal systems, plots of a function of the total gas pressure vs the adsorbed gas yield a straight line. Some data for the sorption of solutes from solutions have been plotted using a Langmuir isotherm approach. Such a treatment probably is only rigorously valid in the case of simple surface adsorption. Plots of radionuclide sorption data or distribution coefficients in the form of Freundlich or Langmuir isotherms are often referred to as empirical isotherms. Sorption on geologic soils or rocks often is much more complex and involves many more factors than those dealt with by these simple idealized relationships; underlying theoretical justification may not exist for constructing such plots. Nonetheless, Freundlich or Langmuir isotherms have proven useful as a means of organizing and presenting sorption data, and they are frequently employed. The greatest limitation lies in the fact that the data usually is a curve and cannot be easily described mathematically or extrapolated to conditions far beyond the region of data.

2.3.6.3 Sorption Potential Energy Isotherms -

The Dubinin-Raduskevich isotherm was developed as a means of obtaining linear plots of sorption values for charcoal (Dubinin and Raduskevich, 1947). It has proven useful for the description of the sorption of sparingly soluble solutes since, unlike the Langmuir or Freundlich isotherms, it does not assume a homogeneous surface, constant adsorption potential, or monolayer surface saturation. In Dubinin-Raduskevich isotherms, the log of the concentration of the adsorbed species is plotted vs a function of the sorption potential energy. Such plots have been utilized to linearize sorption data for radionuclides on basalt (Salter, Ames and McGarrah, 1981a; Ames et al., 1982).

2.3.6.4 Power Exchange Function Isotherm -

The power exchange function isotherm was developed to aid in the prediction of sorption behavior in natural systems where competitive exchange of multiple solutes are important factors in controlling solute sorption (Langmuir, 1981). This isotherm appears not to have been tested with data for radionuclide sorption on candidate repository rocks or minerals. It could be applicable in situations where multiple solute competition could be significant, as in sorption from brine in salt sites.

3 BWIP SORPTION KNOWLEDGE AND INFORMATION NEEDS

3.1 Sorption Issue at BWIP

The Basalt Waste Isolation Project (BWIP) Site Characterization Report (SCR, 1982) has a number of issues and work elements which relate to identifying and quantifying the geochemical conditions and processes affecting radionuclide retardation in the near-field and far-field through repository time. The goal is to develop defensible predictions of potential radionuclide release rates to the accessible environment for various release scenarios and to show that the calculated releases satisfy regulatory requirements. The sorption geochemical process is an important aspect of radionuclide retardation and is the final mechanism or redundant barrier which restricts radionuclide release to the accessible environment following radionuclide solubilization from the waste form in a groundwater-intrusion-canister-breach event. Thus, evaluation and quantification of radionuclide sorption behavior and measurement of radionuclide distribution coefficient and sorption isotherm data are important aspects of BWIP site characterization.

3.2 Summary of Present State of Knowledge

Sorption of radionuclides from groundwater onto near-field and far-field components is an important geochemical process which may substantially retard the radionuclide migration rate, compared to the groundwater migration rate. At the BWIP repository, radionuclides may be adsorbed on host rock and/or backfill primary, secondary, and/or accessory minerals. Considerable information describing sorption on basalt has been developed (Ames and McGarrah, 1980; Barney, 1981; Benson, 1980; Salter, Ames, and McGarrah, 1981a; Salter, Ames, and McGarrah, 1981b; SCR, 1982). Sorption (measured as distribution coefficients or sorption isotherms) was dependent upon the specific basalt minerals, the groundwater composition (ions, Eh, and pH), temperature, and radionuclide concentration and speciation. In general, high distribution coefficients were observed for many radionuclides which may exist as cations, including most actinide species, particularly under repository conditions. However, radionuclides which may be present as anions (such as iodine) showed poor sorption on basalt minerals.

Most of the experimental work was done under oxidizing conditions, although the basalt minerals are expected to establish highly reducing conditions (SCR, 1982). Thus, much of the sorption test results may be of limited application to far-field conditions and modeling, although they may be more directly related to the near-field conditions shortly after repository closure when the engineered system environment may still be oxidizing. The basalt secondary minerals are more prevalent in the interflow and interbed regions of the repository and may be more important to sorption and radionuclide retardation than the primary minerals, although the primary minerals are present in much greater amounts. This is significant since the interflow and interbed regions are more permeable and represent potential groundwater migration pathways and thus secondary minerals may represent the primary sorption medium.

No experimental investigation of multiple speciation effects by column elution methods were described (SCR, 1982), and thus, for actinides (plutonium and neptunium) and fission products like technetium or selenium which frequently display more than one species in solution (i.e., do not readily reach thermodynamic equilibrium), the batch distribution coefficients or sorption isotherms may be only averages of the values for the species present. Multiple speciation effects, if undetected, could introduce substantial errors when the sorption behavior is utilized in performance assessment modeling.

Backfill is the material used to fill the engineered system cavities after waste emplacement. It probably will consist of more than one component in order to meet the dual requirements of restricting the movement of groundwater to the waste canister and of adsorbing radionuclides transported from the waste form after a canister-breach-groundwater-intrusion event (Beall and Allard, 1982; Wood, 1982). The materials presently under consideration are sodium bentonite and crushed basalt (SCR, 1982). Bentonite has advantageous swelling properties in water under ambient conditions, and work is under way to study its properties at the elevated temperatures to be encountered in the near field thermal pulse (SCR, 1982). Uncertainties include the undertermined stability of bentonite to be expected at the thermal and radiation levels to be encountered in the near-field. If the bentonite crystal structure is altered by these conditions, then the desirable swelling properties which restrict the movement of groundwater could be lost with time. The repository host rock has favorable

radionuclide migration sorption properties for cations, and application of crushed basalt (which will be readily available from repository mining operations) is being considered for the backfill material (Wood and Coons, 1982). The effect of crushed basalt on radionuclide sorption is being quantified (Wood and Coons, 1982). Uncertainties may include the not completely defined ability of the crushed basalt to achieve satisfactory sorption under near-field conditions. Basalt may have little effect (i.e., very low distribution coefficients) on some anions such as iodine, and the use of additional backfill components specific for anion retardation may need development (Beall and Allard, 1982).

The near-field basalt mineralogy influences radionuclide sorption by helping establish the parameters such as Eh, pH, solute composition, and surface properties that control the sorption geochemical process. The near-field mineralogy and its influence on radionuclide sorption will be similar to that in the far-field. It will be different from far-field behavior primarily in that higher temperatures (250-300°C) and radiation fields will be involved. Only limited information on the near-field waste package/groundwater/backfill/basalt reactions is available (Benson and Teague, 1979; SCR, 1982). Uncertainties in the waste form, waste load, canister material(s), and backfill component(s) make a definitive analysis of near-field radionuclide sorption difficult at this time. As the engineered system becomes better defined and the system parameters are established, a more precise analysis of near-field mineralogy and its influence on the geochemical processes involved in radionuclide sorption should be completed.

Far-field basalt mineralogy is an important aspect of the repository, since emphasis is given in performance assessment to the ability of the host rock in the far-field to adsorb radionuclides that may be released from the waste package and migrate in groundwater from the near-field. The far-field minerals establish the geochemical parameters for the sorption process. The basalt primary, secondary, and accessory minerals have been well established in most cases (Meyers and Price, 1981; Noonan, Frederick and Nelson, 1980; SCR, 1982). The primary minerals are pyroxene, plagioclase, magnetite, olivine, and interstitial glass. Major secondary minerals formed by subsequent alteration include smectite clay, zeolite, and silica. A variety of accessory minerals are

present, primarily in fractures and vugs. With the exception of the mineral couple responsible for establishing the far-field Eh, little uncertainty remains in the identification of the far-field minerals in the Columbia River basalt flows, although the sorption of radionuclides on these minerals is less well established. More detailed information may be needed on the Umtanum flow mineralogy to exactly define sorption in the repository horizon.

Groundwater chemistry also is important in establishing radionuclide sorption behavior. Considerable information on well water samples from the Pasco basin has been collected and compiled in the Site Characterization Report. However, only very limited information is available for groundwater from the candidate repository horizon. The groundwater conditions (Eh and pH) and ionic composition may be dominated by the mineral species present in the solid adsorbent phase during sorption tests; thus, characterization of the groundwater and quantification of its effect on sorption, while important, may not be as major a concern as solid phase mineralogy. The synthetic groundwaters used in much of the BWIP sorption work may not be representative of expected groundwater in the Umtanum repository horizon. In any case, the migrating groundwater composition may be substantially altered by hydrothermal reactions in the near field. Thus, much of the sorption data may not be directly relevant to anticipated repository conditions in a groundwater intrusion-canister breach scenario.

3.3 Summary of Information Needed to Close the Issue

Considerable additional sorption information may be required in order to close the issue. Batch tests have been carried out under oxidizing conditions to determine distribution coefficients for a number of radionuclides; however, only limited data was reported (SCR, 1982) for reducing conditions. Since considerable emphasis was given in the Site Characterization Report to the strongly reducing nature of the Columbia River basalts, additional distribution coefficient and sorption isotherm data may be needed for the reducing environment expected in the far-field. Also, only limited information for a few radionuclides was reported for sorption measurements under the elevated temperatures (and pressures) to be expected in the near-field. A more extended study of sorption behavior at elevated temperature (up to 250-300°C) would seem desirable in order to model near-field behavior. Such a study should include sorption on backfill

materials as well as basalt primary and secondary minerals. No experimental work was reported with column techniques to test for multiple speciation and its effect on the distribution coefficient value(s) obtained. Such tests would seem to be important for radionuclides such as actinides and certain fission products which are known to be capable of displaying multiple speciation in groundwater systems. Additional work to establish the expected Eh is necessary. Pyrite cannot be assumed to have an important and controlling role unless it can be shown to be widely distributed in the basalt and available for contact with groundwater. Basalt mineralogy questions can probably be closed by resolution of the Eh-controlling couple. The sorption issue cannot be closed until a better understanding of the high temperature sorption, sorption under strongly reducing conditions, expected Eh potential, and multiple speciation effects on distribution coefficients and isotherms has been developed.

Additional information will be required to decrease the wide range of single distribution coefficient values reported (SCR, 1982). Consideration of the potential migration path (interflow and interbed regions) and the specific minerals involved seems desirable. Justification of the emphasis given to various radionuclides is needed to put the sorption work in perspective to anticipated environmental impact. Greater consideration of sorption/desorption disequilibrium should include use of desorption distribution coefficient values when appropriate. Multiple speciation and the use of weighted multiple distribution coefficient values for radionuclides where appropriate may be desirable. The use of single value distribution coefficient values may prove unacceptable due to concentration effects and representation of sorption data by appropriate isotherms, and utilization of these in migration modeling may become necessary. Isotherms derived from fundamental considerations such as the Dubinin-Raduskevich sorption potential energy isotherm or the recent power exchange function isotherm should be considered.

Many of the near-field or engineered system components and/or parameters are not finalized at this time. The waste form may be glass, spent fuel or Synrock, many metals are under consideration as the canister material(s), use of a cast iron overpack has not been resolved, and the composition or even the number of components (including a buffer) of the backfill have not been selected. The waste load has not been established; thus, the thermal pulse magnitude and

radiation exposure of the backfill is uncertain. Information on all these items needs to be finalized before it is possible to establish the information needed to close the issue of radionuclide sorption in the near-field.

Only limited additional information may be required on near-field mineralogy since the near-field and far-field host rock will be similar Columbia River basalts. Basalt mineralogy is relatively well developed. The far-field mineralogy is well established, with the exception of the important question of the mineral couple that controls the system reducing potential or Eh in the reducing environment in the far-field or in the near-field after closure.

3.4 Analysis of Sorption Data Acquisition Plans in the Site Characterization Report

The geochemical process of sorption is not specifically addressed as an issue in the Site Characterization Report (SCR, 1982); however, the need to develop additional sorption data is identified in work elements under Issue W.2.A, "Are the geochemical and hydrologic properties of the geologic setting (in conjunction with the waste forms) sufficient to meet or exceed U.S. NRC proposed waste isolation requirements?", and the utilization of sorption data in modeling and analysis is treated under Issue W.3.A, "Testing and Performance Confirmation." Planned work for additional sorption experiments include investigation of irreversible phenomena and the effect of multiple speciation. Confirmation of the distribution coefficients and sorption isotherms obtained in the laboratory by field migration tests may also be conducted.

The discussion in the Site Characterization Report of plans for future experimental work at BWIP to measure sorption behavior of radionuclides are very brief and thus limit any analysis of their adequacy or likelihood of success. It would be highly desirable if the discussion of the plans could be expanded to include at least the following:

- (1) a discussion of the experimental and analytical techniques to be employed
- (2) identify what Eh conditions are being considered for the test and how the test Eh will be controlled and measured
- (3) specify which radionuclides are to be studied in the sorption tests and how possible multiple speciation is to be evaluated and accommodated in the sorption on data analysis and migration modeling

- (4) state how the mineral and groundwater samples are to be selected for the tests,
- (5) explain how possible sorption/desorption disequilibrium will be investigated.

An expanded discussion of these and similar questions seems desirable in considering future sorption experimental work.

Backfill, its role in helping isolate the waste package from groundwater intrusion, and in adsorbing radionuclides migrating from the waste package to the near-field in a groundwater-intrusion-waste-package-failure event, are thoroughly covered in the Site Characterization Report (SCR, 1982). Issue W.1.B, "Is a unique borehole backfill required?", and the work elements related to this issue, addresses plans to establish backfill requirements and to identify material(s) which will satisfy these requirements. The expected temperature and radiation regime to be experienced by backfill and the water-exclusion and radionuclide-sorption properties needed are addressed in various work elements. The approach appears to be technically sound and seems likely to succeed in developing a satisfactory backfill. The greatest uncertainty which will impact on the likelihood of success lies in the area of the waste form and load. Spent fuel elements, glass or ceramic waste forms could require different backfill materials due to different leaching behavior in the presence of groundwater. Also, the waste load has not been finalized, and this also will influence the backfill requirements and materials. The work elements probably cover a great enough range of possible parameters to develop either a superior backfill which can satisfy all possible situations or a number of backfills for different situations.

Near-field mineralogy and its influence on radionuclide sorption is not specifically addressed as an issue in the Site Characterization Report (SCR, 1982). However, the use of mineralogical information and the impact of mineralogy on the parameters that control geochemical processes and radionuclide sorption are well recognized and identified in a number of work elements which are components of Issue W.1, "Design," Issue W.2, "Site Geochemistry," and Issue W.3, "Testing and Performance Confirmation." Under Issue W.2.A, "Are the geochemical and hydrologic properties of the geologic setting (in conjunction with the waste

forms) sufficient to meet or exceed U.S. NRC proposed waste isolation requirements?", plans for additional petrography and mineralogy activities are identified. Since information on Columbia River basalts is already well developed, the limited additional testing indicated is probably adequate to meet the information needs. More detailed basalt mineralogical data in the near-field vicinity of the planned repository is desirable, but samples for this need can only be obtained after the test shaft is drilled into the Umtanum flow.

Far-field mineralogy and its influence on radionuclide sorption is not specifically addressed as an issue in the Site Characterization Report (SCR, 1982). However, as in the near-field, the use of mineralogical information in determining the parameters which control geochemical processes and radionuclide sorption is well recognized. Plans for resolution of Issue W.2.A, "Are the geochemical and hydrologic properties of the geologic setting (in conjunction with the waste forms) sufficient to meet or exceed U.S. NRC proposed waste isolation requirements?", and Issue W.2.C, "Can valid Eh measurements for the candidate repository horizons in the reference repository location be made either by potentiometric measurement or indirectly by measurement of dissolved redox couples?", address needed additional mineralogical information. Throughout the Site Characterization Report, emphasis was given to the very reducing environment to be expected in the far-field and its favorable effect in limiting expected radionuclide solubilities and, thus, radionuclide migration. Therefore, resolution of the Eh issue is important, in part because emphasis of favorable low anticipated radionuclide solubility (if correct) deemphasizes the expected importance of the radionuclide sorption process.

The present status of Eh information is not completely satisfactory. The plans in Chapter 15 of the Site Characterization Report do not give a clear picture of the future efforts to establish the repository far-field Eh. In-situ Eh measurements at planned repository depth may be very difficult with existing techniques, while water samples raised to the surface and measured there may no longer be representative of the conditions at depth. Estimation of Eh by indirect techniques may introduce calculational uncertainties. It is possible that the specific issue of establishing the repository Eh or expected reducing conditions may not be readily resolved.

4 BIBLIOGRAPHY

Additional discussions of radionuclide sorption on geologic media relevant to waste repository considerations can be found in three excellent recent reports:

ONWI-321, J. B. Moody, Radionuclide Migration/Retardation: Research and Development Technology Status Report, March 1982.

PNL-3997, R. J. Serne and J. F. Relyea, The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program, April 1982.

RHO-BWI-LD-47, G. S. Barney, Evaluation of Methods for Measurement of Radionuclide Distribution Coefficients in Groundwater/Rock Systems, August 1981.

5 REFERENCES

Ames, L. L. and McGarrah, J. E., 1980, Basalt-Radionuclide Distribution Coefficient Determinations, PNL-3146.

Ames, L. L., McGarrah, J. E., Walker, B. A., and Salter, P. F., 1982, "Sorption of Uranium and Cesium by Hanford Basalts and Associated Secondary Smechtite," Chem. Geol. 35, 205-225.

Barney, G. S., 1981, Radionuclide Reactions with Groundwater and Basalts from Columbia River Basalt Formations, RHO-BWI-SA-217.

Barney, G. S. and Anderson, P. D., 1978, Kinetics and Reversibility of Radionuclide Sorption Reactions with Rocks, PNL-SA-7532, Vol. 2, 161-218.

Barney, G. S. and Brown, C. E., 1979, Kinetics and Reversibility of Radionuclide Sorption Reactions with Rocks, PNL-SA-8571, Vol. 2, 261-315.

Barney, G. S. and Wood, B. J., 1980, Identification of Key Radionuclides in a Nuclear Waste Repository in Basalt, RHO-BWI-ST-9.

Beall, G. W. and Allard, B., 1982, Chemical Aspects Governing the Choice of Backfill Materials for Nuclear Waste Repositories, Nucl. Tech. 59, 405-408.

Benson, L. V., 1980, Tabulation and Evaluation of Ion Exchange Data on Smechtites, Certain Zeolites, and Basalt, LBL-10541.

Benson, L. V. and Teague, L. S., 1979, A Study of Rock/Water/Nuclear Waste Interactions in the Pasco Basin, Washington, LBL-9677.

Cleveland, J. M., 1982, Env. Sci. Tech., in press.

Daniels, W. R. and Wolfsberg, K., 1981, Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media, LA-8952-PR.

Davis, J. A., James, R. O., and Leckie, J. O., 1978, "Surface Ionization and Complexation of the Oxide/Water Interface I. Computation of Electrical Double Layer Properties in Simple Electrolytes," J. of Colloid Interface Sci. **63**, 480-499.

Davis, J. A. and Leckie, J. O., 1978, "Surface Ionization and Complexation at the Oxide/Water Interface II. Surface Properties of Iron Oxyhydroxide and Adsorption of Metal Ions," J. Colloid Interface Sci. **67**, 90-107.

Dosch, R. G., 1980, Assessment of Potential Radionuclide Transport in Site-Specific Formations, SAND-79-2468.

Dubinin, M. M. and Radushkevich, L. V., 1947, "Equation of the Characteristic Curve of Activated Charcoal," Proc. Acad. Sci. USSR Phys. Chem Sect. **55**, 331-333.

Erdal, B. R., 1979, Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media, LA-7893-PR.

Erdal, B. R., 1980, Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media, LA-8088-PR.

Erdal, B. R., Daniels, W. R., Hoffman, D. C., Lawrence, F. O., and Wolfsberg, K., 1978, Sorption and Migration of Radionuclides in Geologic Media, LA-UR-78-2746.

Francis, C. W. and Bondiotti, E. A., 1979, Sorption Desorption of Long-Lived Radionuclide Species on Geologic Media, PNL-SA-8571, Vol. 2, 81-133.

Francis, C. W., Reeves, M., Fisher, R. S., and Smith, B. A., 1977, Soil Chromatograph Kd Values, PNL-SA-6957.

Langmuir, D., 1981, "The Power Exchange Function: A General Model for Metal Adsorption onto Geological Materials," in Adsorption from Aqueous Solutions, ed. P. H. Tewari, Plenum Press, 1-17.

Lynch, A. W. and Dosch, R. G., 1980, Sorption Coefficients for Radionuclides on Samples from Water-Bearing Magenta and Calebra Members of the Rustler Formation, SAND-80-1064.

Meyer, R. E., Arnold, W. D., Case, F., Shiao, S. Y., and Palmer, D. A., Valence Effects on Adsorption, ORNL-5905, NUREG/CR-2863, in press.

Moody, J. B., 1981, Radionuclide Migration/Retardation: Research and Development Technology Status Report, ONWI-321.

Myers, C. W. and Price, S. M., 1981 Subsurface Geology of the Cold Creek Syncline, RHO-BWI-ST-14.

Noonan, A. F., Frederickson, C. K., and Nelson, J., 1980, Phase Chemistry of the Umtanum Basalt: A Reference Repository Host in the Columbia Plateau, RHO-BWI-SA-77.

Rafferty, P., Shiao, S. -Y., Binz, C. M., and Meyer, R. E., 1981, "Adsorption of Sr(II) on Clay Minerals: Effects of Salt Concentration, Loading, and pH," J. Inorg. Nucl. Chem. 43, 797-805.

Relyea, J. F. and Serne, R. J., 1979, Controlled Sample Program Publication Number 2: Interlaboratory Comparison of Batch Kd Values, PNL-2872.

Routson, R. C., Barney, G. S., and Smith, R. M., 1981, "Hanford Site Sorption Studies for the Control of Radioactive Wastes: A Review," Nucl. Technol. 54, 100-106.

Salter, P. F., Ames, L. L., and McGarrah, J. E., 1981a, The Sorption Behavior of Selected Radionuclides on Columbia River Basalts, RHO-BWI-LD-48.

Salter, P. F., Ames, L. L., and McGarrah, J. E., 1981b, Sorption of Selected Radionuclides on Secondary Minerals Associated with the Columbia River Basalts, RHO-BWI-LD-43.

SCR, 1982, Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3.

Serne, R. J. Rai, D., and Relyea, J. F., 1979, Preliminary Results on Comparison of Adsorption-Desorption Methods and Statistical Techniques to Generate Kd Predictor Equations, PNL-SA-8571, 63-77.

Serne, R. J. and Relyea, J. F., 1982, The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program, PNL-3997.

Silva, R. J., Benson, L. V., Yee, A. W., and Parks, G. A., 1980, "Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks," in Task 4 Third Contractor Information Meeting, Vol. 1, ed. J. F. Relyea, PNL-SA-8571, 249-355.

Triolo, R., Harrison, N., and Kraus, K. A., 1979, "Use of the Axial Filter to Measure Low Distribution Coefficients," J. Chromatography 179, 19-35.

Vine, E. N., Bayhurst, B. P., Daniels, W. R., DeVilliers, S. J., Erdal, B. R., Lawrence, F. O., and Wolfsberg, K., 1981a, "Radionuclide Transport and Retardation in Tuff," in Scientific Basis for Waste Management, Vol. 3, ed. J. G. Moore, Plenum Press, 483-490.

Vine, E. N., Wolfsberg, K., Bayhurst, B. P., Daniels, W. R., DeVilliers, S. J., Erdal, B. R., and Lawrence, F. O., 1981b, Current Status of Laboratory Sorption Studies, LA-UR-80-3357.

Wood, B. J., 1982, Backfill Performance Requirements - Estimates from Transport Models, Nucl. Tech. 59, 390-404.

Wood, M. I. and Coons, W. E., 1982, Basalt as a Potential Waste Package Backfill Component in a Repository Located Within the Columbia River Basalt, Nucl. Tech. 59, 409-419.

APPENDIX U

**DETERMINATION AND INTERPRETATION
OF SPECIATION AND SOLUBILITIES OF RADIONUCLIDES IN UNDERGROUND
HIGH-LEVEL WASTE REPOSITORIES**

01/27/83

BWIP DSCA/APP U/CORRADO

ABSTRACT

Construction authorization and the licensing of a high-level waste repository involve assessments of the rate of radionuclide migration from the repository and the accumulation of radionuclides at the accessible environment. Knowledge of the expected radionuclide species and the solubilities of radionuclide compounds likely to form under existing groundwater conditions at a repository site, and under conditions of elevated temperature, is essential for assessing radionuclide release rates to the accessible environment. To obtain the solubility data, it will be necessary to identify radionuclide solution species and precipitates that form under the expected range of groundwater conditions, and either to measure their solubilities or demonstrate that sufficient verified thermochemical data are available to confidently calculate the solubilities. This appendix underlines the importance of identifying the species that contribute to solubility and provides guidance for obtaining radionuclide solubility data (and limitations therein) which might be used in support of site characterization, construction authorization, and licensing of a high-level waste repository.

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1.0 INTRODUCTION

1.1 Background

The long-term performance of a high-level waste repository involves geochemical interactions within the geologic repository area among the waste form, backfill, host rock, and groundwater. The rate at which radionuclides may be transported to the accessible environment is a function of:

- (1) waste form leach rates
- (2) diffusion through backfill
- (3) repository conditions (T, P)
- (4) the solubility of each radionuclide present in the waste package
- (5) the radionuclide retardation (chemical reactions of the radionuclides with minerals in the backfill and along flow paths in the host rock)
- (6) the rate and path of groundwater movement
- (7) colloid and polymer formation and transport.
- (8) groundwater composition (Eh, pH, ionic strength, ion concentrations)

Predicting radionuclide transport through geologic systems is complicated by the heterogeneous and complex nature of rock/groundwater interactions. Radionuclides will enter the groundwater as aqueous species whose compositions are determined by waste package and groundwater conditions (pH, Eh, T, and composition). Many radionuclides form complexes of limited solubility with components of groundwaters, and precipitation of stable solid phases might impose an upper limit to the concentration of radionuclides in the groundwater. Conversely, the formation of aqueous species might increase the concentration of a radionuclide in groundwater. Thus, knowledge of the speciation (in site-specific groundwaters) and solubility of the waste form should be determined in order to assess the amounts and release rate of radionuclides from an underground facility. Speciation and solubilities vary with specific conditions at a site, and consideration should be given to changes in (1) waste package due to thermal and radiation damage, (2) backfill due to hydrothermal conditions, (3) host rock due to hydrothermal conditions, and (4) groundwater composition due to hydrothermal conditions.

Geochemical reaction processes that control the residence times of radionuclides in the aqueous phase from the waste canister to the accessible environment include at least the following:

1. Precipitation/dissolution (solubility)
2. Co-precipitation
3. Ion-exchange
4. Simple adsorption
5. Substitution
6. Isotopic exchange

7. Solid-state diffusion (including dead-end pore and matrix)
8. Colloid formation/ultrafiltration
9. Polymer formation

Each of these processes contributes to the overall retardation of radionuclides from the waste package to the accessible environment, and in order to characterize retardation the relative importance of each of these mechanisms must be evaluated. The degree to which each process/mechanism should be studied in characterizing retardation must depend on its relative contribution to the retardation process.

This document is restricted to defining the basic elements of an adequate and acceptable program for determining radionuclide species and solubilities. The scope of this document includes radionuclide species (aqueous) and compounds (precipitates) that might exist within expected ranges of repository conditions between the outer edge of the waste form (following loss of containment) and the accessible environment.

1.2 Regulatory Framework

DOE/EPA/NRC/Responsibilities

The Department of Energy (DOE) has the responsibility for finding and implementing a solution to the high-level waste disposal problem by developing a site for the disposal of high-level waste. Also, DOE is responsible for designing, constructing, and operating the disposal facility. This includes conducting technical development and site characterization programs in geochemistry.

Other Federal agencies that have statutory responsibilities are the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC). EPA's responsibility is to set overall radiological standards for the cumulative release of radionuclides into the environment. The NRC is responsible for licensing a repository to assure public health and safety.

In order for NRC to make construction authorization and licensing decisions, DOE must demonstrate short- and long-term compliance with an EPA standard, which is in proposed status (EPA, 1982). NRC will assess DOE's siting proposals and aspects of their design.

Solubility and speciation investigations are related to the following sections of 10 CFR Part 60:¹

- (a) Section 60.11(a) requires assessment of the site characterization program with respect to investigation activities which address the ability of the site to host a repository and isolate radioactive waste;

¹On July 8, 1981, NRC published proposed technical criteria, and other conforming provisions, for incorporation into 10 CFR Part 60 (46 FR 35280). The adoption of these provisions as final rules was assumed for purposes of preparing this guide. The guide will be modified, as appropriate, to take into account any changes that may be made in the final technical criteria.

- (b) Section 60.21(c) requires that the Safety Analysis Report contain an analysis of the geochemical aspects of the site which bear significantly on its suitability for disposal of radioactive waste;
- (c) Section 60.21(a) indicates that the Commission must determine whether DOE has adequately described the geochemical characteristics of the proposed site prior to granting construction authorization;
- (d) Section 60.111(b) requires that the geologic repository and each of its components satisfy specific requirements related to radionuclide release rates;
- (e) Section 60.122 specifies geochemical conditions at the site which may be considered favorable in their effects on the ability of the site to meet performance objectives;
- (f) Section 60.123 specifies geochemical conditions which might have potentially adverse effects on the ability of the site to meet performance objectives; and
- (g) Section 60.132 specifies additional design requirements for the underground facility which will provide control of radionuclide releases and migration.

The goal of isolating high-level radioactive waste in a repository is to limit the migration of radionuclides from the emplaced waste to the environment at levels low enough to insure that no adverse or unacceptable effects result. Implicit in such a goal is the scientific philosophy that while absolute assurance of zero migration to the environment within geologic times may not be attainable, it is possible to achieve high assurance and reliability of restriction of radionuclide migration to very low and acceptable levels.

The potential amount of geochemical research that can be done in support of high-level radioactive waste isolation is enormous. However, the amount of work is more tractable if research and experiments such as those concerning solubilities are bounded and conducted within expected site-specific ranges of chemical/environmental conditions.

The bounding approach to parameter bracketing should be followed since exact future behavior in a geologic repository over long times may be difficult to quantify precisely. Values of solubility, to be defensible, must limit the actual value only to a range that by conservative judgment establishes that containment, attributed to limited solubility, will be realized. Thus, even though measurement of the precise value may be experimentally complex and difficult or even unattainable, if it can be shown that the value is beyond some bounding limit, this would be sufficient; determination of the precise value, while still desirable, would not be mandatory. This approach to solubility experimental design and execution may substantially simplify the experimental needs.

Similarly, the NRC's geochemistry program is more tractable when it is focused on the following elements:

(1) ISSUES

What are the specific geochemical issues that are important in terms of overall repository performance?

(2) INFORMATION NEEDS

What geochemical mechanisms must be considered in the licensing process and what level of certainty can be placed on them to retard radionuclide migration?

(3) METHODS

What tests, methods, and investigative strategies will be sufficient and appropriate in gathering and interpreting geochemical data?

2.0 DISCUSSION

2.1 General

After loss of containment, radionuclides may enter the local groundwater system. Most radionuclides will react with various components of the groundwater, and the host rock, to form precipitates and sorbing species which will provide a major control on initial radionuclide concentrations. Knowledge of the aqueous speciation of the radionuclides and the solubilities of complexes which they may form is therefore necessary to determine the radionuclide source term from the engineered repository facility.

In order to assess radionuclide speciation, it is necessary to identify (1) waste form and waste package chemistry; (2) the waste inventory; (3) the ligands and chelating agents in the groundwater; and (4) colloids, pseudocolloids, polymers and suspended particulates. Identification of potential radionuclide species can be carried out through adequate characterization of groundwater and substrate (both unaltered and altered).

An assessment of reactions between source radionuclide species and fully characterized groundwater and host rock makes it possible to predict the range of possible species. The species which must be considered can be limited by the use of (Eh, pH) predominance diagram codes such as SOLUPLLOT (Bethke, 1978, Pennsylvania State University Computation Center) which predict (on the basis of thermodynamic principles) which species will dominate in a particular groundwater system as a function of Eh and pH.

The elements of an acceptable program for acquisition of data on the solubility of radionuclide species must involve the compilation of solubility product data for the most probable precipitants of the dominant species (e.g., Rai, Serne, et al., 1980, and Rai, Strickert et al., 1981). Assessment of solubility limits for dominant radionuclide species should be undertaken for the expected range in physical and chemical conditions (e.g., Wood and Rai, 1980, Deutsch et al., 1981, and Rai and Serne, 1978) in order to bound the problem. Assessment of solubility limits should involve laboratory validation of solubility limit data (including technology for characterization of the solid phase, separation of solid and solution phases, and analysis of the aqueous phase).

2.2 Issues

The central issue in this discussion is whether the release of radionuclide species to the accessible environment will result in isotopic concentrations which exceed the EPA (or other adopted) standards.

2.2.1 Speciation

Radionuclides may enter the groundwater system for the first time following loss of containment in simple ionic form, as colloids, as polymers or they may form complexes with ions present in the waste form, in the waste canister, or in the groundwater and the host rock.

A number of long-lived actinides, actinide decay products, and fission products are present in spent reactor fuels and high-level reprocessed waste in sufficient quantities to remain a radiological hazard, even after 1000 years, if placed in an underground repository. The principle isotopes that could represent significant hazards have been identified and are given in Table 1 along with the half-lives and quantities in spent reactor fuel (Arthur D. Little, Inc., 1977). The solid phases and solution species likely to form with the groundwater components depend to a large extent on the oxidation states of the radionuclides. Many of the radionuclides in Table 1 can exist in various oxidation states depending on the redox potential of the groundwaters. The various oxidation states of the radionuclides that might exist under mildly oxidizing or reducing conditions are also given in Table 1.

There will be a number of inorganic components present in the waste package leachate that can form insoluble compounds and solution complexes with the waste radionuclides. For the radionuclides that normally form cations in aqueous solutions, hydroxide, carbonate, sulfate, chloride, fluoride, nitrate, phosphate, silicate, and sulphide would be important groundwater anions. For the radionuclides that normally form anions in aqueous solutions, e.g., Se, Tc, and I, some of the trace metal cations in groundwater could be important, e.g., Cu, Fe, Ag, Hg, and Pb. The potential aqueous speciation of key radionuclides in natural groundwaters is summarized in Table 2 (After Moody, 1982).

2.2.2 Solubility

Concentrations of radionuclide species in solution can increase until they reach an upper limit, the "solubility limit." Above this concentration, a radionuclide species will begin to form a precipitate so that further solution concentration increases do not occur (provided that the rate of precipitation is sufficiently rapid and provided that metastable colloids do not form or that radiolysis does not alter the chemical conditions of the groundwater). In this way, solubility of a particular species provides controls on solution concentrations and migration rates of radionuclides.

Composition of the aqueous phase probably is responsible for more uncertainty in projection of retardation by limited solubility than any other single factor. Compositions of ambient groundwaters of the formation will be altered to an extent difficult to predict by components from leaching of the waste form. Reference forms of glass will introduce boron species and increase silicate contents, as well as other species. Corrosion of the canister will

TABLE 1. Long-Lived Waste Radionuclides *

Isotope	Half-life ⁽³⁾	Quantity ^(b)		Oxidation states
		10 ³ yrs ^(c)	10 ⁴ yrs ^(c)	
⁷⁹ Se	~ 6.5 x 10 ⁴	0.39	0.36	2-, 0, 4+
⁹⁹ Tc	2.1 x 10 ⁵	14.3	13.8	4+, 7+
¹⁰⁷ Pd	~ 7 x 10 ⁶	0.12	0.12	2+
¹²⁶ Sn	~ 10 ⁵	0.56	0.53	2+, 4+
¹²⁹ I	1.7 x 10 ⁷	0.04	0.04	1-, 5+
²¹⁰ Pb	22	0.003	0.12	2+
²²⁶ Ra	1.6 x 10 ³	0.003	0.12	2+
²³⁰ Th	8.0 x 10 ⁴	0.02	0.16	4+
²³⁴ U	2.5 x 10 ⁵	1.92	1.88	4+, 5+, 6+
²³⁵ U	7.1 x 10 ⁸	0.02	0.02	"
²³⁸ U	4.5 x 10 ⁹	0.31	0.31	"
²³⁷ Np	2.1 x 10 ⁶	1.04	1.22	4+, 5+, 6+
²³⁹ Pu	2.4 x 10 ⁴	322	252	3+, 4+, 5+, 6+
²⁴⁰ Pu	6.6 x 10 ³	444	177	"
²⁴² Pu	3.8 x 10 ⁵	1.74	1.71	II
²⁴¹ Am	485	924	0.02	3+
²⁴³ Am	7.7 x 10 ³	15.7	6.94	"

(a) Years

(b) Ci/metric ton of uranium charged to typical PWR(u) reactor

(c) Years after discharge from reactor

* reference?

TABLE 2. Potential Aqueous Speciation of Key Radionuclides in National Ground Waters*

Ion	Species
<u>Simple Anions</u>	: HCO_3^- , CO_3^{2-} I^- , IO_3^- HSe^- , SeO_3^{2-} , SeO_4^{2-} TcO_4^- , MoO_4^{2-} , RuO_4^{2-}
<u>Simple Cations:</u>	: Cs^+ Ni^{2+} , Sr^{2+} , Ra^{2+} , Sn^{2+} , Pb^{2+} , Pu^{4+} , Th^{4+} , Zr^{4+} , Pd^{2+} , Pa^{4+} , U^{4+} , Np^{4+} , UO_2^{2+} , PuO_2^{2+} , NpO_2^+
<u>Complex Ions</u>	:
<u>Ligand</u>	: <u>Simple Cation Forms Mononuclear and/or Polynuclear Species with Ligand to the Left</u>
OH^-	: Ni^{2+} , Sr^{2+} , Sn^{2+} , Am^{3+} , Eu^{3+} , Zr^{4+} , Th^{4+} , Tc^{4+} , U^{4+} , Pu^{4+} , Pa^{5+} , UO_2^{2+}
Cl^-	: Ni^{2+} , Sn^{2+} , Pd^{2+} , Pb^{2+} , Pt^{2+} , U^{4+} , Pu^{4+} , UO_2^{2+} , PuO_2^{2+}
$\text{HCO}_3^-/\text{CO}_3^{2-}$: UO_2^{2+} , PuO_2^{2+} , Th^{4+} , Ni^{2+} , $\text{Tc}^{4+}(\text{?})$, NpO_2^+
SO_4^{2-}	: Eu^{3+} , U^{4+} , Pu^{4+} , Am^{3+} , $\text{Tc}^{4+}(\text{?})$, UO_2^{2+} , PuO_2^{2+}
F^-	: U^{4+} , Pu^{4+} , UO_2^{2+} , PuO_2^{2+} , NpO_2^+
$\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$: UO_2^{2+} , PuO_2^{2+} , NpO_2^+ , U^{4+} , Pu^{4+} , Th^{4+}
<u>Humic & Fulvic</u>	
<u>Acids</u>	: U^{4+} , UO_2^{2+} , Pu^{4+} , PuO_2^{2+} , Ni^{2+} , Pb^{2+} , Th^{4+}

*Modified from Moody (1982).

introduce metal ions. Backfill will also affect the solutions. Grout, if present, may increase carbonate concentrations. Buffers and overpack, if used, could further complicate the composition. If the repository is in a highly soluble matrix, such as salt, the effect on solubility of compositions ranging from saturated in NaCl to brackish, as dilution occurs away from the original formation, must be considered.

Particularly in the immediate vicinity of the waste, alpha, beta, or gamma radiation may cause chemical changes in the aqueous phase. The species introduced by the radiolysis of water could affect solubilities and valence states.

2.3 Information Needs

2.3.1 Basic Elements of Data Acquisition Program

As a first step in identifying potential radionuclide species, it is necessary to know the waste inventory and the ligands (inorganic and organic) present in the groundwater. The latter requirement can be fulfilled by characterizing the groundwater using technically acceptable methods for sampling groundwater, chemical analyses, redox couple measurements, data reduction, statistical analyses, and interpretation. Reactions may be written for speciation of radioelements at appropriate valence states with available ligands. The number of species may be limited by identifying dominant species using an Eh-pH dominance diagram computer code such as SOLUPLOT in conjunction with geochemical speciation codes such as WATEQF, PHREEQE, and MINEQL.

In the assessment of solubility for dominant species, the effect of pH, Eh, and temperature gradients and the chemical and mineralogical environment that extends from the waste canister to the accessible environment, must be considered. Current computer speciation and predominance computer codes should be modified to allow data corrections for ionic strength and elevated temperature. Thermodynamic calculations using solubility product and species dissociation constant data can be used to determine the maximum concentrations in solution of given radioisotopes under a range of conditions. Laboratory validation of solubility data should include the interlaboratory comparison of data using technically acceptable methods for characterization of the solid phase, separation of solid and solution phases, and analysis of the aqueous phase.

Therefore, basic elements of an acceptable program for generating speciation and solubility data will include: (1) the characterization of initial groundwater conditions, (2) interlaboratory comparisons of groundwater chemistry, (3) determination of anticipated (altered) groundwater chemistry conditions, (4) determination of speciation and solubility, and (5) assessment of speciation and solubility data through peer review, interlaboratory comparisons, and validated computer models.

2.4 Methods

2.4.1 Approach for Characterization of Groundwater

A complete characterization of groundwater will be required. Sampling and analyses should be coordinated to meet the data needs of both the hydrological and the geochemical issues being addressed at a site.

In order to predict the nature of possible solution species and precipitates of radionuclides likely to form in groundwaters, it is necessary to know the ranges of chemical compositions, and pH and redox properties of representative, uncontaminated groundwater samples. A detailed chemical analysis of major and trace components (including organics) is necessary. An analysis of colloids and particulates in otherwise undisturbed groundwater must also be made to ensure that radionuclides will not be transported by colloids and particulates present in the water.

Colloids are stabilized against coagulation largely by electrostatic repulsion arising from charges on their surface. With oxides, surface charge will be heavily dependent on pH and on the presence of ions which may exchange with surface hydroxyls. In general, positive surface charge (anion-exchange capacity) decreases with increasing pH, and negative surface charge (cation-exchange capacity) increases with pH. Whether or not oxides are dispersed in the liquid strongly depends on solution composition. In general, increasing electrolyte concentration tends to destabilize colloidal dispersions, and the presence of multivalent ions of sign opposite to surface charges also destabilizes (unless they are adsorbed strongly enough to reverse charge sign). Three aspects of colloid and particulate transport are: (1) What is the concentration of colloids and particulates? (2) Will radiocolloids form in groundwater otherwise free of colloids and particulates? and (3) How significant is the contribution of colloids and particulates in transporting radionuclides?

Because many radionuclide metal ions form both insoluble compounds and solution complexes with the anions of typical groundwater (for example, hydroxide, sulfide, sulphate, carbonate, phosphate, silicate, chloride, fluoride and nitrate anions), the identities and concentrations of groundwater anions are needed. The radionuclide anions, selenide and iodide, can form insoluble compounds and aqueous complexes with several of the heavy metals (e.g., Fe, Mn, Ni, Co, Cu, Ag, Hg, and Pb) found at trace levels in groundwaters. Therefore, trace element concentrations should be determined. In addition, mixed compounds containing radionuclides and major groundwater cations may form, e.g., $(Ca (UO_2)_2 (H_2SiO_4)_2)^{-6}$; thus concentration of the major cations should be measured.

The oxidation states of the waste radionuclides will determine the nature of the precipitates likely to form and the solubilities of these compounds will, in part, determine solution concentrations. In order to predict these oxidation states, knowledge of the redox properties of the groundwater/host rock system is required. The pH range must be known because solubility and adsorption are functions of pH. Experiments to determine the likely pH range in the thermally disturbed zone should also be undertaken.

Also, if compositionally different groundwaters are to be present in the repository and/or within the waste package (backfill/canister/waste form) due to chemical changes induced by the engineered system at the time of loss of containment or to thermally induced reactions, then these altered waters will have to be taken into account when determining source-term speciation/solubility.

2.4.1.1 Chemical Methods for Determining Groundwater Composition

A number of analytical methods are available for determining the concentration of major and trace elements, as well as anions, in water samples. They include

neutron activation analysis, fluorimetry, emission spectroscopy (particularly inductively coupled plasma), atomic absorption spectroscopy (both flame and non-flame), atomic fluorescence spectroscopy, electrometry, and ion-exchange chromatography. Since the utility, detection limits, and reliability of the various methods differ for different elements, no single method can be recommended for a complete chemical analysis of a water sample. The choice of methods usually depends on the instruments that are available and on the concentrations of the components to be measured and the level of precision needed. The analytical methods listed above are well established, and the procedures, advantages, limitations, and precautions have been discussed in a number of publications (e.g., Winefordner, 1976; Pinta, 1978; Wood, 1976; 1970; Ellis, 1968).

Precision and sensitivities of analytical techniques have increased to such an extent in recent years that the weakest links in the analysis are the procurement of uncontaminated samples, and the subsequent handling and preparation of samples. Therefore, certain precautions should be observed and certain procedures followed to insure reliable results (e.g., Wood, 1976; Brown, 1970; Ellis, 1968). A system of checks to assure that contamination is not occurring during different stages of sample handling should be built into the analytical procedures.

A sufficient number of replicate samples should be analyzed to establish the consistency of sample preparation and the accuracy of measurements. Because discrepancies between different analytical methods for some elements at low concentrations arise from differences in sample preparation techniques, and what is measured (e.g., dissolved and suspended particulates, or dissolved alone), it is desirable to analyze for some elements by two or more alternative methods.

Checks should be made to test the internal consistency of the analyses. These checks should include tests of chemical and electrical balance, reconciliation of alkalinity titrations with CO_2 measurements and pH, and reconciliation of solution composition with the nature of the contacting geologic media. However, these tests provide only approximate indications of the validity of the analyses. Large deviations can indicate a large error in one or more of the determinations, but consistency is not conclusive proof that each determination is accurate.

2.4.1.2 Redox Measurements

The redox potential affects the oxidation state that a given element will be found in, and as the chemical properties of an element depend very much on its oxidation state, variations in redox potentials may have a profound influence on the migration properties of a radionuclide.

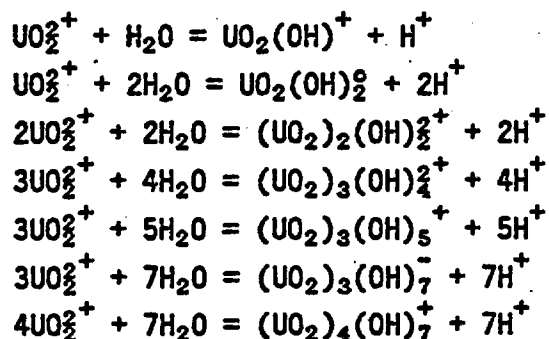
The Eh of water samples is almost always measured using an electrode (platinum) and a reference electrode system using a sensitive voltmeter. This type of direct measurement of Eh for geologic purposes is beset with a number of experimental problems and limitations (e.g., Garrels and Christ, 1965; Langmuir, 1971; Stumm and Morgan, 1971; Benson, 1980; Morris, 1967). Also, in theory it is possible to evaluate the redox potential in natural waters by determining the relative concentrations of members of some or all of the redox couples in the system provided that the system is in equilibrium.

For the initial characterization of Eh an attempt should be made to obtain the necessary data on the groundwater composition to calculate Eh values for the major redox couples. If these values are reasonably self consistent, it may only be necessary to verify the results by direct measurement of the oxidation states of a few selected multivalent radionuclides.

2.4.2 Approach for Characterization of Solubility

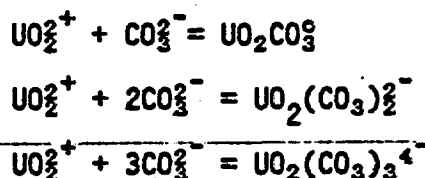
To predict the solution concentrations of radionuclides that will occur in a repository/groundwater system, two different approaches can be taken. One method is to calculate solution concentrations from independent thermochemical data (i.e., those based on calorimetric measurements) on solubility product constants and solution complexation constants. A recent review of this approach is summarized in Edelstein et al. (1983). The other method is direct measurement. (In fact, these two approaches are fundamentally related because "independent thermochemical data" is obtained from laboratory measurements.)

In order to predict solution concentrations of radionuclides in a repository/groundwater system, the identities and solubilities of the solid phases and identities of the solution species likely to form under specific groundwater/geologic conditions are needed. Solubility product constants alone are usually not sufficient to predict solution concentrations because the formation of hydrolysis products and other complexes increases apparent solubilities. For example, one can predict the concentration of UO_2^{2+} in solution in equilibrium with solid $\text{UO}_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$ from the solubility constants and the association constants of the following equations:



hydrolysis

All of these equations must be solved simultaneously in order to calculate the concentrations of the individual solution species since they can occur together in solution. In addition, if other solution complexes are present they must be included. For example, if carbonate is present in the uranium bearing system, reactions involving the carbonate complexes of uranyl must be included, i.e.,



The formation of insoluble phases and their equilibria with solution species are much more complicated processes in natural systems than in those normally

encountered in laboratory measurements. Since the waste radionuclides would most likely be present at low concentrations in the contaminated groundwaters, it is reasonable to expect that they would behave in a manner similar to other trace elements. Trace elements usually occur in nature as major components of discrete accessory minerals, and as solid solutions with mineral phases formed by more abundant elements or "co-precipitates" with the precipitates formed by more abundant elements. Unfortunately, complete thermodynamic information on most relevant accessory minerals and solid solutions does not exist for any of the waste radionuclides in natural systems. Therefore, it is not possible at present to calculate the course of such complicated reactions for these radionuclides. In situ experiments with the waste radionuclides to obtain the necessary thermodynamic data would be either extremely difficult or impossible to carry out. In cases where needed data are not available, the stability constants of complexes of important radionuclide cations with important groundwater anions must be determined experimentally at 25°C. The radionuclides studied should at a minimum include those identified as being of greatest significance under the EPA standard. The ligands studied should at a minimum include OH⁻, Cl⁻, HCO₃⁻, CO₃²⁻, SO₄²⁻, F⁻, H₂SiO₄⁻, HSiO₄²⁻, SiO₄³⁻, H₂PO₄⁻, PO₄³⁻, H₂BO₄⁻, HBO₄²⁻, BO₄³⁻, HNO₃⁻, and NO₃²⁻.

The stability constants for selected, important complexes should be determined up to at least 175°C and for anticipated solution ionic strength. These complexes should be chosen with consideration of the results obtained above. In addition, improved methods for correlating and predicting the stability constants of complexes should be developed (Baes and Mesmer, 1981).

What can be done more readily is to consider the solubilities of simple or pure compounds of the waste elements that can form with groundwater components under conditions of temperature, Eh and pressure characteristics of the repository environment (both antecedent and post-waste emplacement). This is a conservative approach because from thermodynamic considerations, compounds or minerals of higher free energy tend to convert to compounds or minerals of lower free energy, i.e., solid phases will continuously change to phases having lower solubilities. Thus, in principle, upper limits of radionuclide concentrations in solution could be estimated.

The second approach for determining the effects of the formation of insoluble compounds on solution concentrations of radionuclides is direct measurement of the solution concentrations as functions of the initial radionuclide concentration over the range of solution compositions, temperature, Eh, pH, and other parameters expected for the repository groundwater. The problem with this approach is that fundamental thermodynamic data would not be obtained to extrapolate to possible future conditions of the repository system beyond the range of parameters studied. However, if available thermodynamic data were used to predict solubilities and the direct measurement were used to test these predictions, then the careful characterization of the solid phases and solution species produced in such solubility measurements would greatly enhance the utility of the information.

2.4.2.1 Solubility Measurement Methods

Measurement of the solubility of a compound in aqueous solution involves basically the following steps: formation or preparation of the solid phase,

characterization of the solid phase, separation of the solid and aqueous phases, and analysis of the aqueous phase for the dissolved species. The most commonly used method for determining solubility is first to prepare the compound by some standard procedure. The material is characterized and then an excess of the solid is placed in contact with an aqueous solution of the appropriate composition. Some of the solid phase dissolves and the system is allowed to come to equilibrium before the aqueous phase is analyzed for the concentration of the element of interest and the precipitating counter-ions. From the concentrations, a solubility product can be calculated, after due account is taken of speciation and ionic strength.

A second, but less commonly used method involves the preparation of an aqueous solution containing both the element of interest and the precipitating counter-ion at concentrations that produce a supersaturated solution with respect to precipitation of the compound. There may or may not be pre-prepared solid phases present. Again, the system is allowed to come to equilibrium and the aqueous phase analyzed.

(Note: Both the undersaturation and supersaturation approaches described here assume that the solid phases form and dissolve stoichiometrically. In other words, it is assumed that any precipitate that forms is the end member of a solid phase series and not a metastable phase exerting a temporary control on the solubility.)

For reliable results, it should be demonstrated that equilibrium has been achieved in solubility measurements. The most rigorous method of demonstrating that a solubility experiment has reached equilibrium is to approach equilibrium from both undersaturated and supersaturated conditions, i.e., a combination of the two methods discussed above. The inability to duplicate solubility measurements from undersaturated and supersaturated conditions would require an explanation and identification of mechanisms responsible for the lack of agreement.

2.4.2.1.1 Separation of Solid and Solution Phases

The compounds of many of the long-lived radionuclides that are likely to form in natural systems are very insoluble, and very low solution concentrations of the radionuclides would be expected, e.g., 10^{-8} to 10^{-12} M. However, some radionuclides, especially the actinides, can form colloidal suspensions which, if included in the analysis of the solution phase, could lead to large errors in the solubility measurement.

The separation of solid and solution phases is an important step in the analysis. Techniques often employed for separating the solution and solid phases in solubility studies include (1) gravitational settling, (2) centrifugation, (3) filtration, or a combination of all three methods. In the first method the solid phase is simply allowed to settle for an extended period of time before a portion of the aqueous phase is withdrawn for analysis. This method could allow suspended or colloidal material to be withdrawn as well. Centrifugation induces and enhances gravitational settling. However, there is little information on the minimum time or revolution speed needed to achieve adequate separation. Filtration can be used as a final or single separation step. The use of two or three filters with decreasing pore sizes in the range of 0.4 to 0.15 micron (and smaller for colloidal particles) to filter the same sample would be needed, and care should be taken since there is some evidence that filters themselves may at times adsorb

soluble species from solution and that different materials and different filter constructions behave differently in this respect (Polansky, 1977). Finally, whatever method or combination of methods is used, verification of the effectiveness of the separation will be needed.

The question of the evaluation of the effect of colloidal material on mobility of nuclides is more difficult. On route is to analyze solution samples both before and after removal of fines. Migration rates of samples of the two down a column of representative geologic material could then be measured. A faster rate for a significant portion of the sample from which fines had not been removed would signal caution in estimates of confinement of the nuclide.

2.4.2.1.2 Characterization of Solid Phase

Characterization of the solid phase used in making a solubility determination is of utmost importance. When using a compound prepared under one set of solution conditions, it cannot be automatically assumed that the prepared compound is the controlling solid phase without confirmation. In complex aqueous solutions such as groundwaters, a second, more stable solid phase may form that could control the solubility of the element of interest. Also, when preparing a sparingly soluble compound according to an established procedure, the exact composition and structure of the solid will vary depending on a number of factors, including kinetics, temperature, solution concentrations, and the age of the precipitate. Furthermore, the solid phases may change from an "active" to an "inactive" form during the course of the experiment, i.e., a free energy change is associated with the conversion of an amorphous or finely divided crystal precipitate into a well crystallized solid.

- The active form of a precipitate consists of very fine crystals with disordered crystal lattices. Such a precipitate may persist in metastable equilibrium with the solution and may be converted only slowly into a more stable and inactive form (Stumm and Morgan, 1981; Alard, 1981; Feitknecht and Schindler, 1963). Conversely, radiation damage to oxide precipitates of high-specific-activity nuclides may affect precipitation and dissolution kinetics. Loss of crystallinity of Am(III) and Cm(III) is an example (Haire, et al., 1977) of the effects that might occur. Measurements of the solubility of "active" forms give solubility products that are higher than those of the inactive forms (Zimmerman, 1952; Baes, 1976), and provide data relevant to a worst-case analysis.

Finally, the particle size of the solid phase is a factor in determining the solubility of a compound. In general, the equilibrium concentrations of dissolved products decrease as the average particle size increases, so special precautions on this point are sometimes needed (Zimmerman, 1952; Baes, 1976).

It can be questioned in some cases whether the large-crystal stable phases assumed are indeed those present at the lowest free energy of the system under conditions of contact with aqueous phases in formation. Large surface areas of fine simple crystals such as BaSO_4 have substantial interfacial energy, and larger particles will consequently grow at the expense of small crystals; the well-known higher solubilities of finely divided solids than of large crystals correspond to this. However, particularly with hydrous oxides and other oxides of many of the elements of interest here, high ion-exchange capacities, of the

order of an equivalent/kg solid under some conditions (Kraus, et al., 1958; Amphlett, 1964) imply that there may be negative contributions to overall free energy with increasing surface area for particles in some size ranges.

Aging studies of Pu(IV) oxide (Haire, et al., 1971) illustrate the persistence of small particle sizes. Amorphous hydroxide precipitated by ammonia from nitrate solution, dialyzed to 0.1 nitrate/Pu and, after evaporation, thermally denitrated at 100°C resulted in cubic PuO₂ particles of 40 to 100 Å, or 80 to 100 Å at 250°C. If large PuO₂ crystals are the most stable form, the kinetics of reaching it may be very slow in aqueous modes. Microcrystals of 100 Å range might have about 20% of the atoms on the surface, available for exchange reactions between surface hydroxides and ions in solution.

X-ray or electron diffraction is recommended for the characterization of crystalline precipitates. Crystal structure and stoichiometry can usually be determined by this method if a sufficiently large single crystal is available and a good quality chemical analysis is available. Frequently, only a finely divided crystalline precipitate is available and characterization is made by comparison of powder patterns with those of known compounds of chemically related elements. Through this method, conclusions can be drawn as to the chemical activity or degree of crystallization of the precipitate from broadening of the lines (Feitknecht and Schindler, 1963). It is very difficult, however, to characterize the crystal structure using this method. Amorphous precipitates cannot be analyzed by these means and characterization must be made through elemental analysis of the solid. While this type of analysis often can identify the nature and stoichiometry of the solid phase, it provides no structural information and, thus, no information on the active form of the solid. Elemental analysis usually requires milligram amounts of material that may not be available, and techniques for the characterization of small amounts of precipitates absorbed on surfaces, as might be the case in natural systems, would require scanning transmission electron microscopy. Solution techniques such as infrared spectroscopy might be useful for analysis of bonding in fine amorphous precipitates.

2.4.2.1.3 Characterization of the Aqueous Phase

A number of analytical methods are available for determining the concentrations of the dissolved species. The particular method to be used depends on the element and its expected concentration. Since the radionuclide concentrations may be quite low, rather sensitive methods need to be employed. In the past, the most commonly used method included radiochemical techniques, potentiometry, polarography, colorimetry, and atomic absorption spectroscopy. Generally speaking, these methods are adequate for concentrations in the range of parts per million. More recently, improvements in neutron activation analysis, emission spectroscopy, and fluorescence spectroscopy have lowered the sensitivity range to parts per billion. All of these methods are well established and their advantages and limitations have been discussed in detail (Winefordner, 1976; Pinta, 1978).

3.0 ASSESSMENT OF SOLUBILITY CALCULATIONS FOR HANFORD BASALT FLOWS

This chapter provides an assessment of the solubility discussions and conclusions contained in Chapter 6 of the BWIP Site Characterization Report

(SCR). The emphasis of the assessment is on the SCR comparison of estimated solubilities for actinide compounds $\text{UO}_2(\text{c})$, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{N}_2\text{O}_2(\text{c})$, $\text{PuO}_2(\text{c})$, and Am (soil) with Maximum Permissible Concentrations (NRC, 1982) presented in Section 6.4.1 and Figure 6-15 of the SCR. We take exception to SCR conclusions (pages 6.4-3 to 6.4-5) that:

"Based on solubility, the maximum possible release rates for all the radionuclides considered will be below the NRC 10^{-5} proposed release criterion (NRC, 1981) and the draft cumulative release criterion (EPA, 1981). Although the extrapolation of the solubility data (obtained under oxidizing conditions and estimated based on available thermodynamic data) to reducing conditions indicates that uranium, neptunium, americium, and plutonium would be maintained close to or well below the maximum permissible concentration limits (Figure 6-15), experimental validation is needed."

Based on currently available thermodynamic data of Allard (1982) and MINEQL data (Table 8), we find that the concentrations of uranium, neptunium, americium, and plutonium may exceed the maximum permissible concentration limits (MPC) by several orders of magnitude under anticipated ranges of basalt repository Eh-pH and groundwater compositions. It appears that carbonate complexation and to a lesser extent fluoride, sulfate and silicate complexation in BWIP groundwater greatly increases the solubilities of these four actinides. Therefore, the SCR is not justified in ignoring the effects of common groundwater ligands, polymers, and colloids on actinide solubility.

Further, we caution that it is premature to determine based on solubilities whether maximum possible release rates for U, Np, Am, and Pu will be below the NRC 10^{-5} proposed release rate criterion and the EPA draft cumulative release criteria. The actual solubilities for these actinides, and therefore release rates, will greatly exceed values reported in the SCR since the values reported in the SCR do not consider the presence of the common inorganic ligands found in BWIP groundwaters under the expected range of repository Eh-pH and temperature. In addition, the potential for increases in groundwater concentrations of these actinides, due to colloid formation, the formation of actinide polymers, organic complexation, supersaturation and reaction kinetics, and temperature are not yet fully understood and, therefore, have not been considered by BWIP in their conclusions presented in Chapter 6 or Chapter 11 of the SCR.

→ We agree that experimental validation of solubility measurements is required. Experimental determinations of solubility are often in disagreement. According to Allard (1982), "what appears to be oversaturated solutions can be due to slow kinetics in the formation, e.g., thermodynamically stable oxides, or due to the existence of colloidal particulates not in true solutions. By the presence of oxide or silicate surfaces, on the other hand, species in solution will be adsorbed in certain pH-ranges, leading to a lower concentration in solution." A considerable experimental effort involving interlaboratory comparisons will be required to reduce uncertainties in important thermodynamic constants. Nevertheless, a significant body of thermodynamic data on actinides has been generated in the last several years which allow preliminary estimates of actinide solubilities.

Finally, we should point out that comparisons of the solubilities of the actinides to MPC are useful in the sense that they provide an indirect means of comparing solubility as a "barrier" versus an "index of health effects." However, for the purposes of licensing a high-level waste repository, the final published rules by NRC (10 CFR Part 60) and EPA (40 CFR Part 191) will apply, not NRC Maximum Permissible Concentration limits (10 CFR Part 20).

3.1 Approach

The approach normally taken to establish releases of groundwater contaminants requires the characterization of the chemistry and environmental conditions of the groundwater, groundwater flow rates at representative locations in the groundwater system, and the solubility of the contaminant in the system. The input requirements also require a detailed analysis of the substrates which occur along fractures and in porous zones so that the extent to which the contaminants will be retarded by reversible or irreversible reactions among contaminants, groundwater, and substrates can be estimated (e.g., see Miller and Benson, 1983, In Press). At present the groundwater chemistry, flow rates, substrate characteristics, and radionuclide solubilities in Hanford groundwater are insufficiently known to allow an adequate analysis of radionuclide migration rates in Hanford groundwaters. In addition, an adequate analysis requires that the leach rates of waste forms are known for anticipated repository conditions, especially temperature, Eh-pH, and ionic strength, as well as the species that will be released to the groundwater system at the waste package-groundwater interface. Given the absence of this required information RHO has adopted the more simplified approach of bounding the problem. However, the bounds that they have set on solubility are not conservative. Given the lack of data, we have assessed the solubility discussions by focusing on the assumptions made by the BWIP staff and via preliminary solubility estimates.

3.2 Maximum Permissible Concentration (MPC)

The calculations presented in Section 6.4.1 and Figure 6-15 of the SCR make use of outdated MPC data (NRC, 1981). The basis for the MPC values published in Appendix B of 10 CFR Part 20 are outdated with the release of new ICRP values (ICRP Publication 30). We have made a preliminary estimate of the adjusted MPCs on the basis of the new ICRP-30 data and compare these to the old values in Appendix B of 10 CFR Part 20 (Table 3). The calculation assumes an average daily water intake of 2200 cm³ and a factor of 10 for nonoccupational exposures. In every case, the adjusted values are more restrictive by about 1 to 2 orders of magnitude. Thus, this adjustment will raise the solubility to MPC ratio in Table 6-15 of the SCR by 1 to 2 orders of magnitude.¹

As noted in the introduction, comparisons of solubilities to MPC are only indirectly useful since NRC 10 CFR Part 60 and EPA 40 CFR Part 191, not NRC 10 CFR Part 20 are applicable for establishing postclosure constraints on releases from high-level waste repositories.

¹NRC staff are currently revising Appendix B of 10 CFR 20. They will account for health effects on children in the population. This will result in smaller MPC values than the ones presented here.

TABLE 3. Comparison of 10 CFR Part 20 and ICRP 30 MPCs

Element	Isotope	<u>$\mu\text{Ci/ml}$</u>	<u>$\mu\text{Ci/ml}$</u>
		10 CFR 20(2)	ICRP-30(3)
Am	Am ²⁴¹	4×10^{-6}	1.7×10^{-7}
	Am ²⁴³	4×10^{-6}	1.7×10^{-7}
Pu	Pu ²³⁹	5×10^{-6}	6.7×10^{-7}
	Pu ²⁴⁰	5×10^{-6}	6.7×10^{-7}
	Pu ²⁴²	5×10^{-6}	1.0×10^{-6}
Np	Np ²³⁷	3×10^{-6}	1×10^{-8}
U	U ²³⁴	4×10^{-5}	1.4×10^{-6}
	U ²³⁶	3×10^{-5}	1.7×10^{-6}
	U ²³⁸	3×10^{-5}	1.7×10^{-6}

1. *Calculated assuming an average daily water intake of 2200 cm³ (ICRP II) and a factor of 10 for non-occupational exposures.
2. Code of Federal Regulations Chapter 10, Part 20, Appendix B, Revised January 1982.
3. Limits for Intakes of Radionuclides by Workers, ICRP Publication 30, Pergamon Press, New York, 1978.

The Maximum Permissible Concentrations for the isotopes of U, Np, Pu, and Am considered in the SCR in uncontrolled discharge (in terms of moles/liter) are presented in Table 4. The data for the initial inventory, the inventory at 1,000 years, and for Ci/mole are from Wood and Rai (1981), the reference used in the SCR estimates. The moles/liter for the nuclides are calculated assuming isotopic equilibrium (as they were in Wood and Rai, 1981). The moles/liter calculations also account for the new ICRP-30 data.

3.3 Solubility Data

The calculations presented in Section 6.4.1 and Figure 6-15 of the SCR are misleading in that they do not discuss how the lack of consideration of carbonate complexation might affect their calculations. A review of current literature (Allard, 1982) and experimental work on the actinides (Cleveland, 1982) indicate that the complexation of actinides by carbonate greatly increases actinide solubilities.

Allard has recently summarized literature on the solubilities of actinides in neutral or basic solutions. He has calculated solubilities of U, Np, Pu, and Am in the pH range 5-11 for oxidizing and reducing conditions in the presence of carbonate. The results of the Allard calculations are presented in Figures 2 and 3. The relevant solubility values for the oxidizing and reducing cases are selected from these figures at pH 9.5 and are divided by the corrected MPC values (Table 5) so that they can be compared to the calculations presented in Figure 6-15 of the SCR. Allard estimated the solubilities for a total carbonate concentration of 7.9×10^{-3} M and for Eh = +0.26 volt (oxidizing case) and for Eh = -0.36 volt (reducing case). These values are comparable to values for Hanford groundwaters reported in the SCR: total carbonate concentration of about 2.6×10^{-3} M; Eh = +0.22 to -0.45 volt.

Comparison of the solubility to MPC ratios presented in the BWIP SCR with Allard solubilities to MPC (adjusted from ICRP 30) indicate large apparent discrepancies. These discrepancies were identified for all the nuclides of Am, Pu, Np, and U reported in the BWIP SCR for both oxidizing and reducing conditions (Table 6 and Figure 1). Most of the ratios differed by 5 or more orders of magnitude, a level of disagreement which would introduce an unacceptable level of uncertainty and risk into contaminant release scenarios.

The Allard (1982) estimates of solubility are also subject to considerable uncertainty because: (1) best estimates were made for key thermodynamic data where none exist; and (2) there remains considerable disagreement among reported values for key thermodynamic data. Many of these discrepancies are discussed in Allard (1982).

3.4 MINEQL Calculations

In order to substantiate that complexation by carbonate is important in estimating actinide solubilities, several preliminary solubility calculations were made using MINEQL at Lawrence Berkeley Laboratories. The solution conditions used in the MINEQL calculations are presented in Table 7. The calculations were carried out for U, Np, Pu, and Am using the reactions and constants given under thermodynamic data (Table 8). The MINEQL calculations presented below are not intended to represent an accurate assessment of the

Table 4. Projected Total Inventory of High-Activity Constituents of Spent Fuel in the United States^a (after Wood and Rai, 1981)

Nuclide	Initial Inventory (Ci)	Inventory at 1000 yr (Ci) ^b	Ci/Mole	Mole Fraction	MPC ^c Moles/Liter
²³⁴ U	7 x 10 ³	7.4 x 10 ⁴	1.4	.001	4.8 x 10 ⁻¹⁰
²³⁶ U	1 x 10 ⁴	3 x 10 ⁴	1.4 x 10 ⁻²	.006	4.8 x 10 ⁻⁸
²³⁸ U	3 x 10 ⁴	3 x 10 ⁴	8 x 10 ⁻⁵	.994	8.4 x 10 ⁻⁶
²³⁷ Np	3 x 10 ⁴	1 x 10 ⁵	0.2		2.4 x 10 ⁻¹¹
²³⁹ Pu	2.8 x 10 ⁷	2.7 x 10 ⁷	15	.68	3.1 x 10 ⁻¹¹
²⁴⁰ Pu	4.2 x 10 ⁷	3.8 x 10 ⁷	54	.26	8.7 x 10 ⁻¹²
²⁴² Pu	1.5 x 10 ⁵	1.5 x 10 ⁵	0.9	.06	5.2 x 10 ⁻¹⁰
²⁴¹ Am	1.5 x 10 ⁸	7.8 x 10 ⁷	780	.79	8.6 x 10 ⁻¹⁴
²⁴³ Am	1.3 x 10 ⁶	1.2 x 10 ⁶	45	.21	1.5 x 10 ⁻¹²

^aBased on 93,000 metric tons of heavy metal, the estimated 10-year-old spent fuel inventory in the year 2010.

^bChange in inventory due to radioactive decay.

^cMPC calculated from ICRP 30 assuming 2200 cm³ average daily water intake and a factor of 10 for nonoccupational exposures.

Table 5. Allard Solubilities/MPC (ICRP 30)

	Solubility/MPC	Ratio
U ²³⁸ ox	$10^0/8.4 \times 10^{-6}$	1.2×10^5
U ²³⁶ ox	$6 \times 10^{-3}/4.8 \times 10^{-8}$	1.3×10^5
U ²³⁴ ox	$1.4 \times 10^{-4}/4.8 \times 10^{-10}$	2.9×10^5
U ²³⁸ red	$3 \times 10^{-3}/8.4 \times 10^{-6}$	3.6×10^2
U ²³⁶ red	$1.8 \times 10^{-4}/4.8 \times 10^{-8}$	3.8×10^3
U ²³⁴ red	$2 \times 10^{-8}/4.8 \times 10^{-10}$	4×10^2
Np ²³⁷ ox	$10^{-1}/2.4 \times 10^{-11}$	4.2×10^9
Np ²³⁷ red	$10^{-8}/2.4 \times 10^{-11}$	4.2×10^2
Am ²⁴¹ both	$7.9 \times 10^{-6}/8.6 \times 10^{-14}$	9.2×10^7
Am ²⁴³ both	$2.1 \times 10^{-6}/1.5 \times 10^{-12}$	1.4×10^6
Pu ²³⁹ ox	$6.8 \times 10^{-9}/3.1 \times 10^{-11}$	2.2×10^2
Pu ²⁴⁰ ox	$2.6 \times 10^{-9}/8.7 \times 10^{-12}$	3×10^2
Pu ²⁴² ox	$0.6 \times 10^{-9}/5.2 \times 10^{-10}$	1.2×10^0
Pu ²³⁹ red	$6.8 \times 10^{-8}/3.1 \times 10^{-11}$	2.2×10^3
Pu ²⁴⁰ red	$2.6 \times 10^{-8}/8.7 \times 10^{-12}$	3×10^3
Pu ²⁴² red	$0.6 \times 10^{-8}/5.2 \times 10^{-10}$	1.2×10^1

TABLE 6. Comparison of BWIP SCR and Allard Radionuclide Solubility/MPC

I Nuclide	II Eh	III BWIP SCR (MPC from 10 CFR 20)	IV Allard (MPC from ICRP 30) Column III	Disagree- ment (MPC from ICRP 30) Column IV/ Column III
^{241}Am	both ox, red		10^{-6}	10^8
^{243}Am	both ox, red		10^{-4}	10^{10}
^{242}Pu	ox		10^{-5}	10^0
^{242}Pu	red			10^1
^{240}Pu	ox		10^{-3}	10^2
^{240}Pu	red			10^3
^{239}Pu	ox		10^{-3}	10^2
^{239}Pu	red		10^{-1}	10^3
^{237}Np	ox		10^1	10^9
^{237}Np	red		10^{-11}	10^2
^{234}U	ox		10^{-1}	10^5
^{234}U	red		10^{-4}	10^2
^{236}U	ox		10^{-1}	10^5
^{236}U	red		10^{-4}	10^3
^{238}U	ox		10^{-1}	10^5
^{238}U	red		10^{-4}	10^2

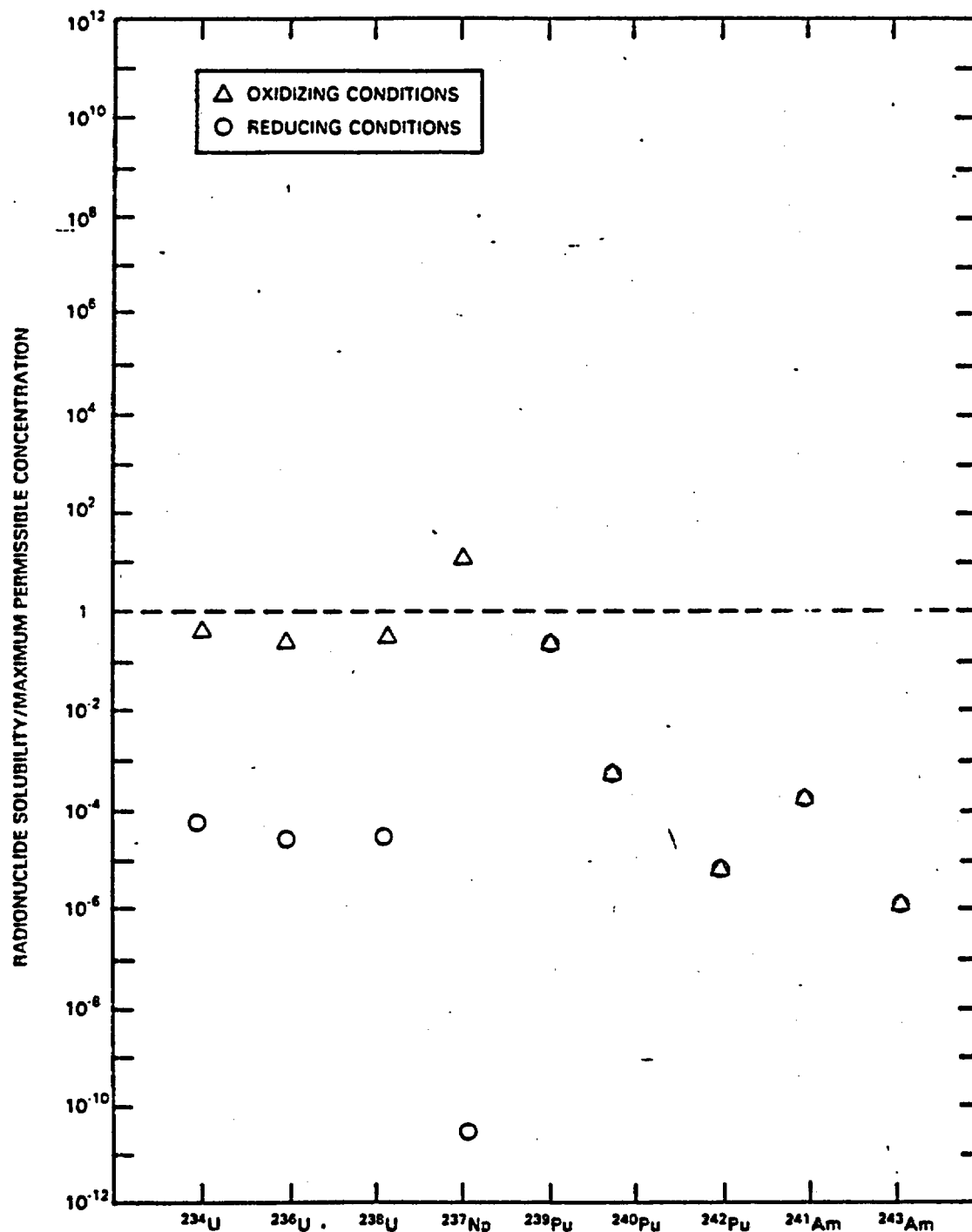
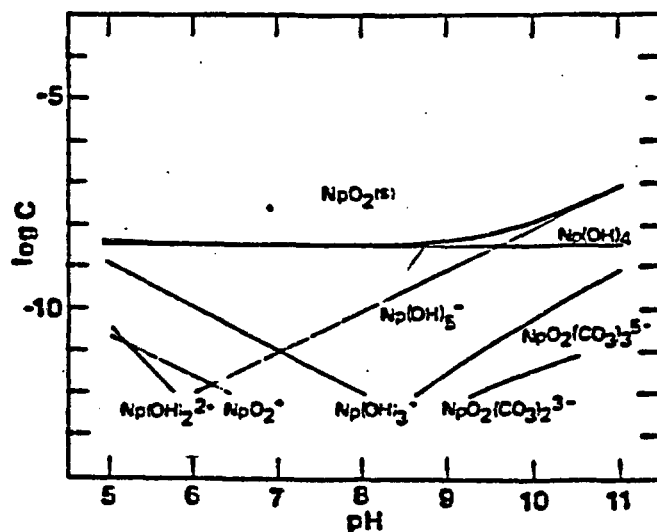
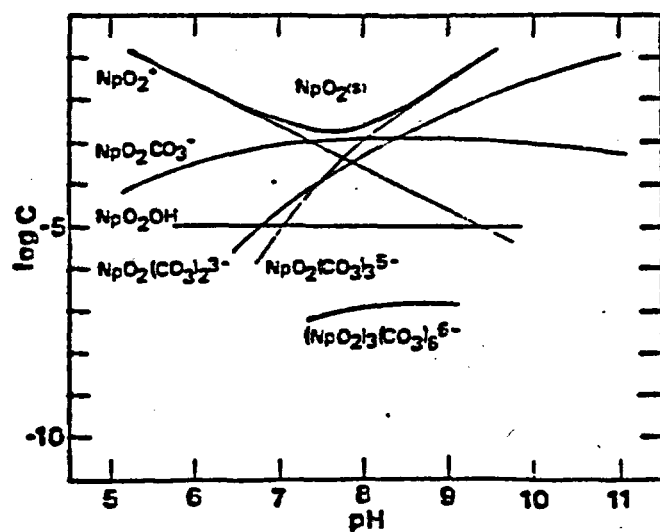
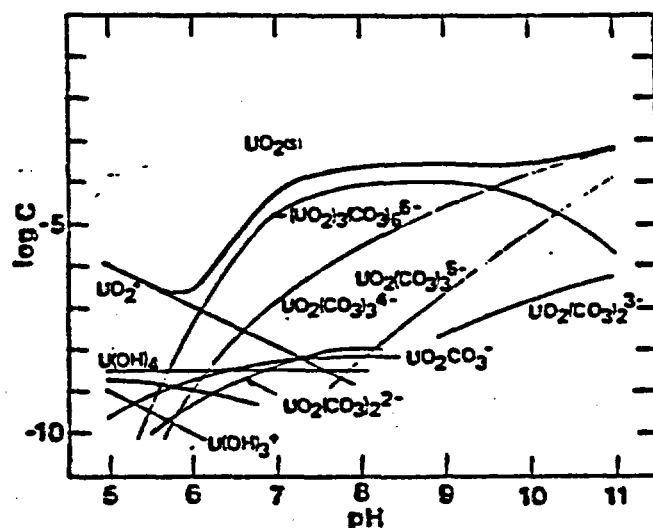


Figure 1. Comparison of BWIP SCR and Allard Radionuclide Solubility versus MPC. BWIP SCR Data Calculated for Actinide Compounds $\text{UO}_2(\text{c})$, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{Np}_2(\text{c})$, $\text{PuO}_2(\text{c})$, and Am (soil) with the Maximum Permissible Concentrations (NRC, 1981) Under Respository Conditions of 25°C, 0.1 Megapascal, pH 10, and Eh 0.29 Volt (oxidizing) or -0.27 Volt (reducing). Allard values are presented in Tables 1 - 4 and Figures 2 and 3. Allard values are plotted as solid triangles (oxidizing) and circles (reducing).



Neptunium solubilities (M) and species in solution $\Sigma \text{CO}_3 = 7.9 \times 10^{-3} \text{ M}$;
 Eh = 0.8 - 0.06 pH (figure c);
 Eh = 0.2 - 0.06 pH (figure d).

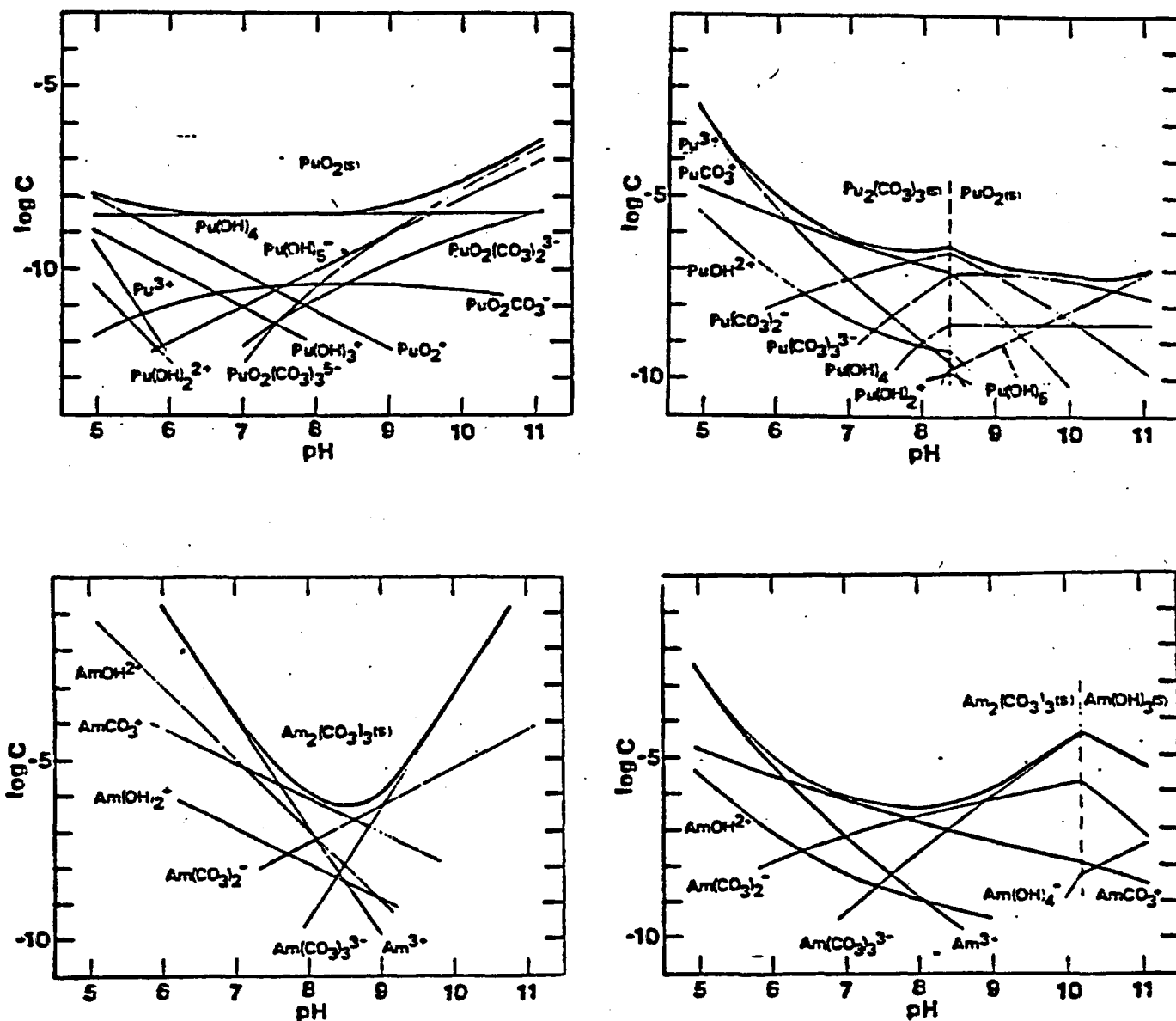


Figure 3. Plutonium solubilities (M) and species in solution $\Sigma \text{CO}_3 = 7.9 \times 10^{-3} \text{ M}$;
 $\text{Eh} = 0.8 - 0.06 \text{ pH}$ (figure a);
 $\text{Eh} = 0.2 - 0.06 \text{ pH}$ (figure b).

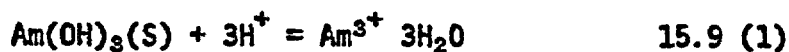
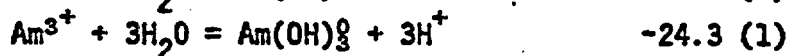
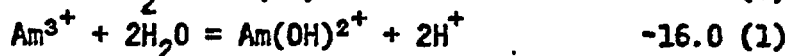
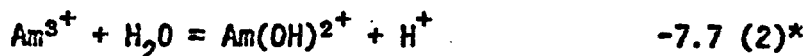
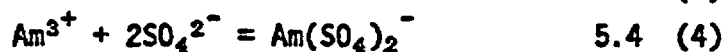
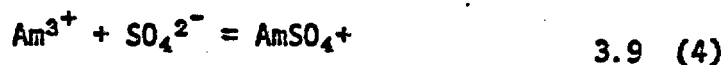
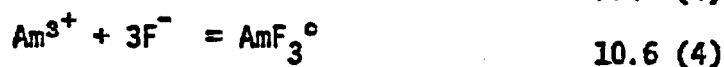
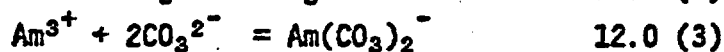
Americium solubilities (M) and species in solution $\text{P}(\text{CO}_2) = 10^{-3.5} \text{ atm}$
 (figure c) and
 $\Sigma \text{CO}_3 = 7.9 \times 10^{-3} \text{ M}$ (figure d);
 $\text{Eh} = 0.08 - 0.06 \text{ pH}$ and $\text{Eh} = 0.2 - 0.06 \text{ pH}$.

TABLE 7. Solution Conditions for MINEQL Calculations

<u>Components</u>	<u>ppm</u>	<u>moles/liter</u>
F ⁻	42	2.2×10^{-3}
SO ₄ ⁼	199	2.1×10^{-3}
Cl ⁻	297	8.4×10^{-3}
Total Carbonate	157	2.6×10^{-3}

Eh = +0.21 and -0.22 Volt
 pH = 6 to 10 in 0.5 unit steps

TABLE 8 Thermodynamic Data

I. Am^{3+} (25°C, $\mu = 0$)PrecipitatesLog KHydrolysisComplexes

II. Pu

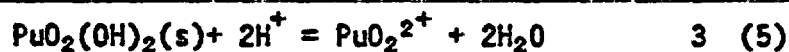
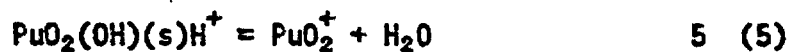
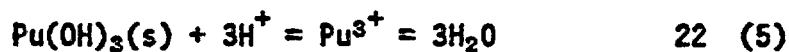
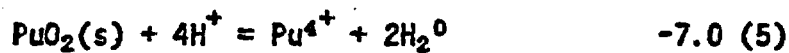
PrecipitatesLog K* values for Cm^{3+}

TABLE 8 (Continued)

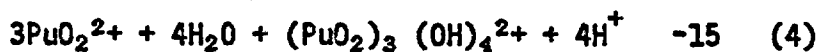
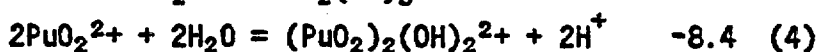
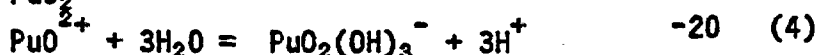
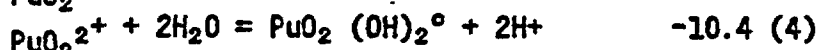
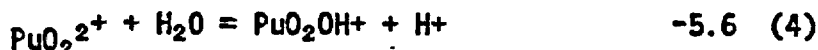
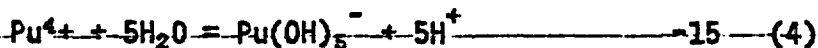
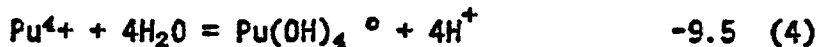
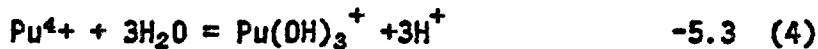
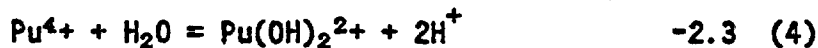
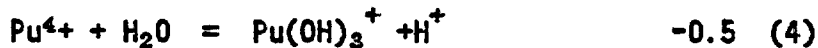
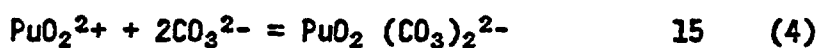
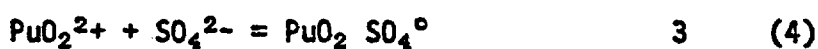
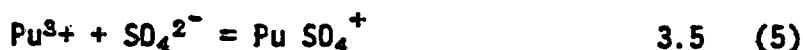
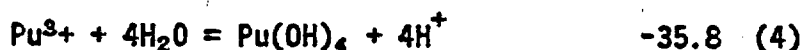
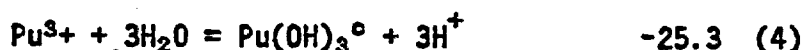
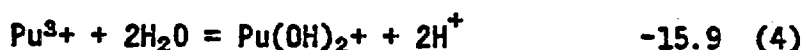
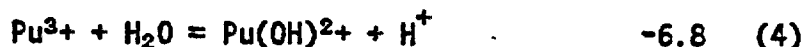
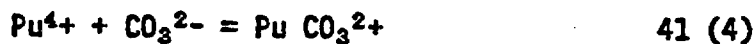
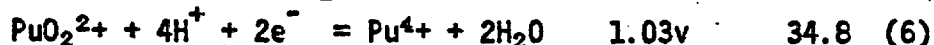
ComplexesLog K

TABLE 8 (Continued)

Log KRedox Reactionsstd. pot (E°).Log K

III. Np

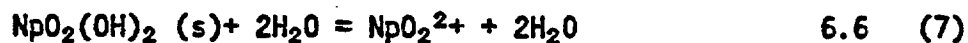
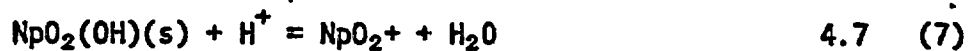
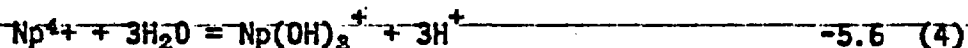
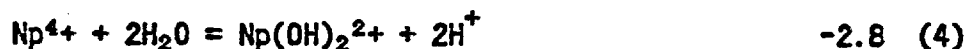
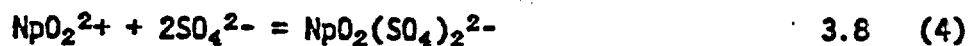
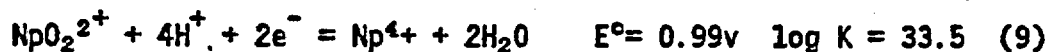
PrecipitatesComplexesLog K

TABLE 8 (Continued)

$\text{Np}^{4+} + \text{Cl}^- = \text{NpCl}^{3+}$	1.2	(4)
$\text{Np}^{4+} + 2\text{Cl}^- = \text{NpCl}_2^{2+}$	1.9	(4)
$\text{Np}^{4+} + 3\text{Cl}^- = \text{NpCl}_3^+$	2.3	(4)
$\text{Np}^{4+} + \text{F}^- = \text{NpF}^{3+}$	8.3	(4)
$\text{Np}^{4+} + 2\text{F}^- = \text{NpF}_2^{2+}$	14.5	(4)
$\text{Np}^{4+} + 3\text{F}^- = \text{NpF}_3^+$	20.3	(4)
$\text{Np}^{4+} + 4\text{F}^- = \text{NpF}_4^0$	25.1	(4)
$\text{Np}^{4+} + \text{SO}_4^{2-} = \text{Np}(\text{SO}_4)^{2+}$	5.5	(4)
$\text{Np}^{4+} + 2\text{SO}_4^{2-} = \text{Np}(\text{SO}_4)^0$	8.5	(4)
$\text{Np}^{4+} + \text{CO}_3^{2-} = \text{NpCO}_3^{2+}$	41	(4)*
$\text{NpO}_2^+ + \text{Cl}^- = \text{NpO}_2\text{Cl}$	-0.1	(4)
$\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH} + \text{H}^+$	-8.85	(4)
$\text{NpO}_2^+ + 2\text{H}_2\text{O} = \text{NpO}_2(\text{OH})_2^- + 2\text{H}^+$	-18	(4)
$\text{NpO}_2^+ + \text{CO}_3^{2-} = \text{NpO}_2(\text{CO}_3)^-$	5.9	(8)
$\text{NpO}_2^+ + 3\text{CO}_3^{2-} = \text{NpO}_2(\text{CO}_3)_3^{5-}$	16.3	(8)
$\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH}^+ + \text{H}^+$	-5.15	(4)
$\text{NpO}_2^{2+} + 2\text{H}_2\text{O} = \text{NpO}_2(\text{OH})_2^0 + 2\text{H}^+$	-10.2	(4)
$\text{NpO}_2^{2+} + 3\text{H}_2\text{O} = \text{NpO}_2(\text{OH})_3^- + 3\text{H}^+$	-19	(4)
$2\text{NpO}_2^{2+} + 2\text{H}_2\text{O} = (\text{NpO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-6.39	(4)
$3\text{NpO}_2^{2+} + 4\text{H}_2\text{O} = (\text{NpO}_2)_3(\text{OH})_4^{2+} + 4\text{H}^+$	-13	(4)
$3\text{NpO}_2^{2+} + 5\text{H}_2\text{O} = (\text{NpO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-17.5	(4)
$\text{NpO}_2^{2+} + \text{F}^- = \text{NpO}_2\text{F}^+$	4.6	(4)
$\text{NpO}_2^{2+} + 2\text{F}^- = \text{NpO}_2\text{F}_2^0$	7.7	(4)
$\text{NpO}_2^{2+} + \text{SO}_4^{2-} = \text{NpO}_2\text{SO}_4^0$	3.27	(4)

*Based on value for PuCO_3^{2+}

TABLE 8 (Continued)

Redox Reactions

IV. U

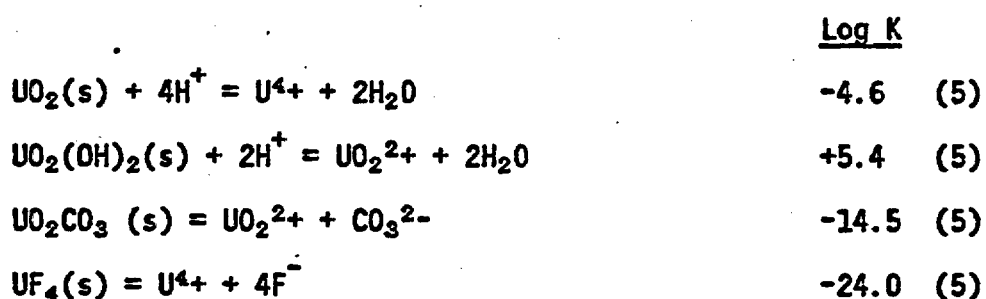
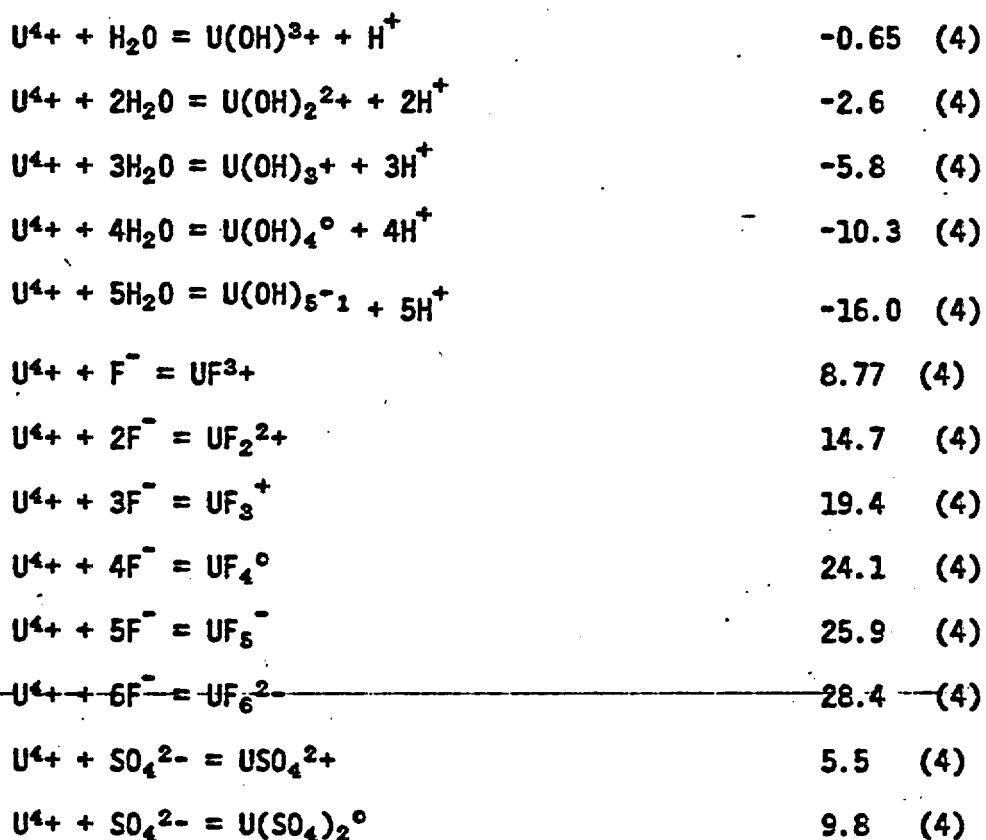
PrecipitatesComplexes

TABLE 8 (Continued)

$U^{4+} + Cl^{-} = UCl^{3+}$	1.5 (4)
$U^{4+} + CO_3^{2-} = UCO_3^{2+}$	41 (4)
$UO_2^{2+} + H_2O = UO_2OH^{+} + H^{+}$	-5.5 (10)
$UO_2^{2+} + 2H_2O = UO_2(OH)_2^{\circ} + 2H^{+}$	-11.9 (10)
$2 UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^{+}$	-5.89 (10)
$3 UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^{+} + 5H^{+}$	-16.5 (10)
$3 UO_2^{2+} + 4H_2O = (UO_2)_3(OH)_4^{2+} + 4H^{+}$	-12.3 (10)
$3 UO_2^{2+} + 7H_2O = (UO_2)_3(OH)_7^{-} + 7H^{+}$	-22.8 (10)
$4 UO_2^{2+} + 7H_2O = (UO_2)_4(OH)_7^{+} + 7H^{+}$	-30.8 (10)
$UO_2^{2+} + CO_3^{2-} = UO_2CO_3^{\circ}$	7.50 (4)
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.7 (4)
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	20.9 (4)
$UO_2^{2+} + SO_4^{2-} = UO_2SO_4^{\circ}$	2.95 (4)
$UO_2^{2+} + 2SO_4^{2-} = UO_2(SO_4)_2^{2-}$	4.28 (4)
$UO_2^{2+} + 3SO_4^{2-} = UO_2(SO_4)_3^{4-}$	4.70 (4)
$UO_2^{2+} + Cl^{-} = UO_2Cl^{+}$	0.21 (4)
$UO_2^{2+} + F^{-} = UO_2F^{+}$	5.16 (4)
$UO_2^{2+} + 2F^{-} = UO_2F_2^{\circ}$	8.85 (4)
$UO_2^{2+} + 3F^{-} = UO_2F_3^{-}$	11.42 (4)
$UO_2^{2+} + 4F^{-} = UO_2F_4^{2-}$	11.97 (4)

Redox Reactions

$UO_2^{2+} + e^{-} = UO_2^{+}$	$E^{\circ} = .163v.$	$\log K = 2.75 (6)$
$UO_2^{2+} + 4H^{+} + 2e^{-} = U^{4+} + 2H_2O$	$E^{\circ} = .273v.$	$\log K = 9.22(6)$

*Based on value for $PuCO_3^{2+}$

References to Table 8

- (1) Silva, R. J., 1982, "Solubilities of crystalline Nd and Am Trihydroxides," ONWI Topical Report, LBL-15055.
- (2) Bucher, J. and N. Edelstein, 1982, "Hydrolysis and Solubilities of Cm(III), Nd(III) and Np(V)." ONWI Topical Report, LBL-15056.
- (3) Lundquist, R., 1982, "Hydrophilic Complexes of the Actinides I. Carbonates of Am and Eu," Accepted for publication in Acta Chemica Scandinavica.
- (4) Phillips, S. L., 1982, "Hydrolysis and Formation Constants at 25°C," LBL-___, (Presented in part, 183rd National ACS meeting, Las Vegas, NV, March 26-April 2, 1982.
- (5) Lemire, R. S. and P. R. Tremaine, 1980 "Uranium and Plutonium Equilibria in Aqueous solutions to 200C," Chem. Eng. Data, Vol. 25, pp. 361-370.
- (6) Fuger, J. and F. L. Oetting, 1976, "The Chemical Thermodynamics of Actinide Elements and Compounds - Part 2 - The Actinide Aqueous Ions," I.A.E.A., Vienna, 65 pp.
- (7) Baes, C.F. and R.E. Mesmer, 1976, The Hydrolysis of Cations, Juiley and Sons, NY, p. 184.
- (8) Nitsche, H. and N. Edelstein, 1982, "Carbonate Complexation of Np(V) in Near Neutral and Basic Solutions," ONWI Topical Report, LBL-14935.
- (9) Burney, G. A. and R. M. Harbour, 1974, Radiochemistry of Neptunium, National Academy of Sciences, National Research Council, NAS-NS-3060, U.S. Tech. Info. Service, U.S. Dept. of Commerce, Springfield, VA, p. 23.
- (10) Silva, R. J. and A. W. Yee, 1982, "Uranium (VI) Retardation Mechanisms," Earth Science Division Annual Report 1981, LBL-13600, pp. 45-47.

solubility limits of U, Np, Pu, and Am in Hanford groundwaters. Discrepancies in some of the available dissociation and hydrolysis constants and missing data do not permit definitive estimates at this time. However, they do illustrate that lack of consideration of important complexes (e.g., carbonates) can result in serious underestimates of solubility.

3.4.1 Uranium

In our uranium calculations the limiting solid phase for the oxidizing case is schoepite [$\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$]. The uranium in solution is in the U(VI) state and is dominated by carbonate and hydroxyl complexes. The important ligands in descending order of importance are $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $(\text{UO}_2)_3(\text{OH})_2^-$, and $\text{UO}_2(\text{OH})_2^-$. Although fluoride, chloride, and sulfate species were considered in this analysis, they did not make a significant contribution to the solubility of uranium. The results of the MINEQL estimates are presented in Figure 4a. The calculated solubility for uranium is $\log C = -2.7$ moles/liter at: $\Sigma\text{CO}_3 = 2.6 \times 10^{-3}$ moles/liter, $\text{pH} = 9.5$ and $\text{Eh} = +0.21$ volts.

The limiting solid phase for the reducing case is uraninite [$\text{UO}_2(\text{s})$]. The total uranium in solution is in the U(IV) state and is dominated by the UCO_3^+ complex. The results of the MINEQL estimates are presented in Figure 4b. The calculated solubility for uranium is $\log C = -5.1$ at: $\text{pH} = 9.5$, $\Sigma\text{CO}_3 = 2.6 \times 10^{-3}$ moles/liter, and $\text{Eh} = -0.22$ Volt. Coffinite [USiO_4] may be an important solubility limiting phase under reducing conditions but dissolved silica was not included in our estimates.

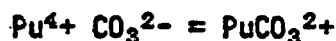
A number of the important uranium constants reported in the literature will require further research to reduce uncertainties.

The disagreement between our calculations and those of Allard (1981) result from differences in the value of the formation constant selected for $(\text{UO}_2)_3(\text{CO}_3)_6^-$. We elected to use the value reported by Ferri et al. (1981) which was not corrected to zero ionic strength ($\log K = 41.5$). Allard corrected the same value to zero ionic strength ($\log K = 60.5$) resulting in much higher values for uranium solubility. We believe that there is insufficient information to allow correction of the Ferri et al. value to zero ionic strength. If the actual value of the constant is higher, then our estimated solubilities are too low.

A significant discrepancy in the reported value for the hydrolysis constant, $\text{U}(\text{OH})_5^-$, also needs to be resolved. The $\log K$ values range from -16 (Baes and Mesmer, 1976) to -13 (Lemire and Tremaine, 1980). If the -13 value is correct then our estimated solubilities are too low.

3.4.2 Neptunium

The limiting solid phase for the oxidizing and reducing cases is $\text{NpO}_2(\text{s})$. Since the 4+ species for Np, U, and Pu could be important, we used Lemire and Tremaine's (1980) estimate for:



U-25

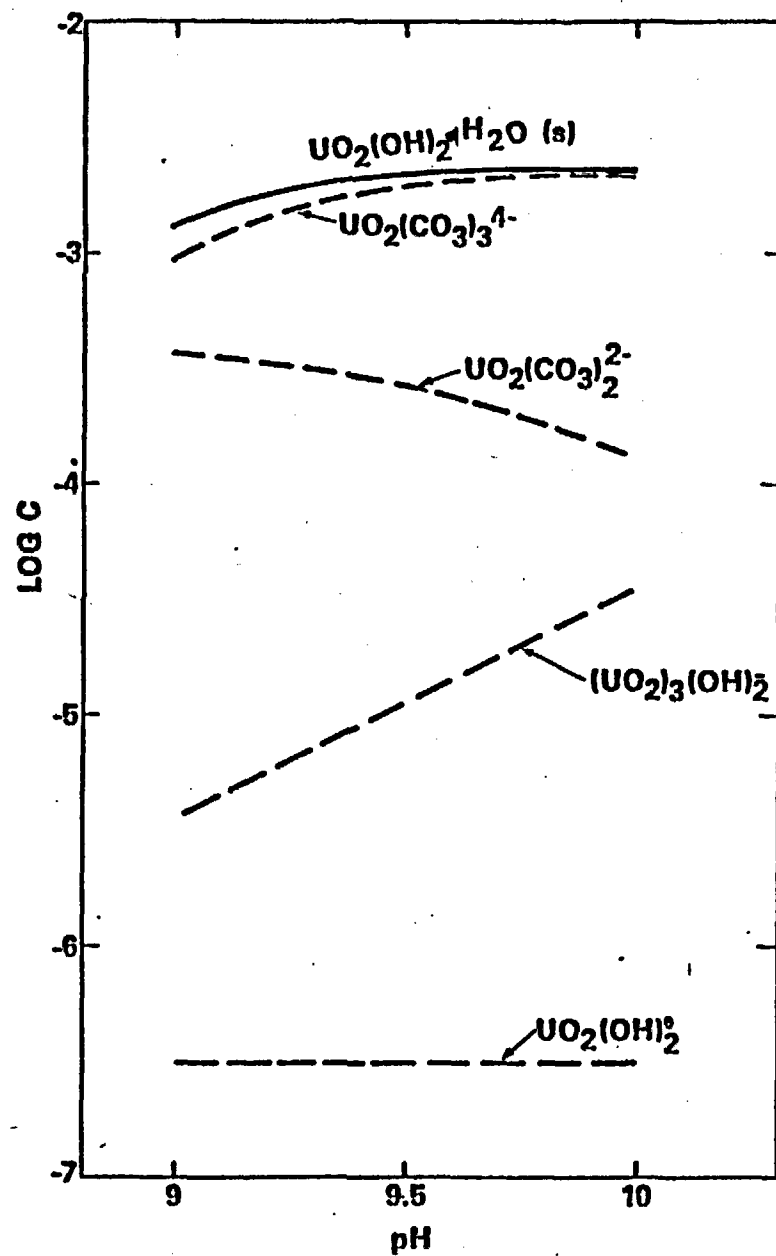


Figure 4a

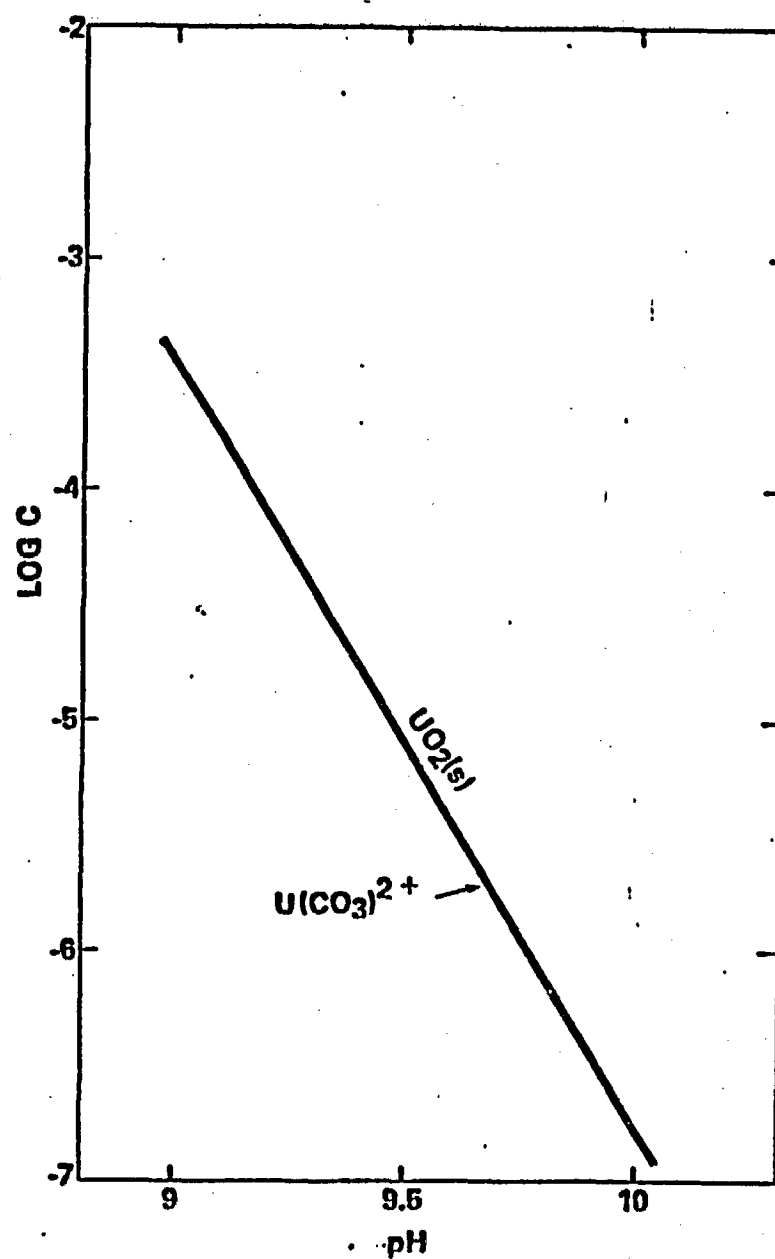


Figure 4b

that
of $\log K = 41$ and assumed the same value for UCO_3^{4+} and $Np_2CO_3^{2+}$ in the absence of any other data. Lemire and Tremaine (1980) indicate that the free energy of formation they report is a lower limit and may overestimate the stability of the $PuCO_3^{2+}$ complex which would result in an overestimation in our Pu and Np estimates.

In the oxidizing case both the tetravalent and pentavalent species, $Np(CO_3)_2^{2+}$ and $NpO_2(CO_3)_3^{5-}$ are important whereas in the reducing case only the tetravalent complex is important (Figures 5a and 5b). There are no data on the carbonate complexes of Np(VI) but they could only make neptunium more soluble. The MINEQL estimates for neptunium are $\log C = -4.5$ moles/liter for both the oxidizing (+0.25V) and reducing (-0.22V) for: $\Sigma CO_3 = 2.6 \times 10^{-3}$ moles/liter, $pH = 9.5$.

3.4.3 Americium

The only oxidation state that would be obtained under ambient in situ conditions in BWIP repository waters would be the trivalent state (Figure 6a). Therefore, the limiting solid phase for $Eh = +0.21V$ to $-0.22V$ is $Am(OH)_3(s)$. Carbonate and hydroxyl complexes control americium solubility from pH 9 to 10 however, contributions are also made by fluoride and sulfate complexes. The MINEQL estimate for americium solubility at $pH = 9.5$ is $\log C = -7.5$ moles/liter for $\Sigma CO_3 = 2.6 \times 10^{-3}$ moles/liter, F-concentration of 2.2×10^{-3} moles/liter and SO_4^{2-} concentration of 2.1×10^{-3} moles/liter.

3.4.4 Plutonium

The limiting solid phase for both the oxidizing (+0.21V) and reducing (-0.22V) cases is $PuO_2(s)$. The only important ligand for the oxidizing and reducing cases is $PuCO_3^{2+}$. The MINEQL estimate for plutonium solubility of $pH = 9.5$ is $\log C = -7.0$ moles/liter for $Eh = +0.21V$ and $-0.22V$, $\Sigma CO_3 = 2.6 \times 10^{-3}$ moles/liter.

Several experimental solubility measurements have been reported for crystalline $PuO_2(s)$ (Grenthe and Ferri, 1981, $\log K_s = -55.8$; and Rai, Serne, and Moore, 1980 $\log K_s = -52$). Solubility-lattice correlations by Baes and Mesmer (1976) yield a $\log K_s = -63$. According to Allard (1982)

"the observed solubility of e.g., $PuO_2(s)$ can vary substantially depending on crystallinity, stoichiometry, presence of lattice defects, presence of impurities, condition of formation and existence of various modifications."

and therefore we have chosen the $\log K_s = -63$ whereas, Allard uses the $\log K_s = -54$ value. This is an important discrepancy which will require resolution through additional research. If the $\log K_s = -54$ value chosen by Allard is correct then our estimated solubility is too low.

Thermodynamic data for $PuCO_3^{2+}$ will require further research. Lemire and Tremaine (1980) indicate that the free energy of formation that they report is a lower limit that may overestimate the stability of this complex. If this is true then our estimates of plutonium solubility are too high.

22-n

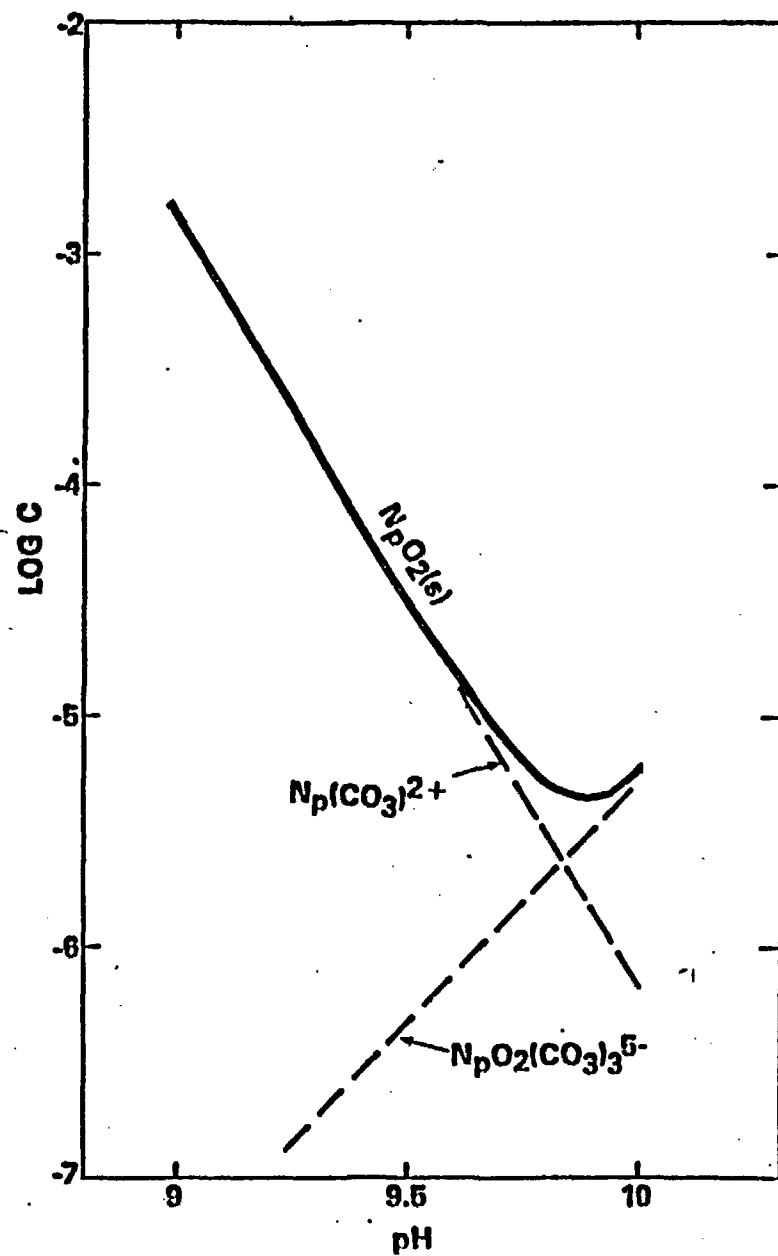


Figure 5a.

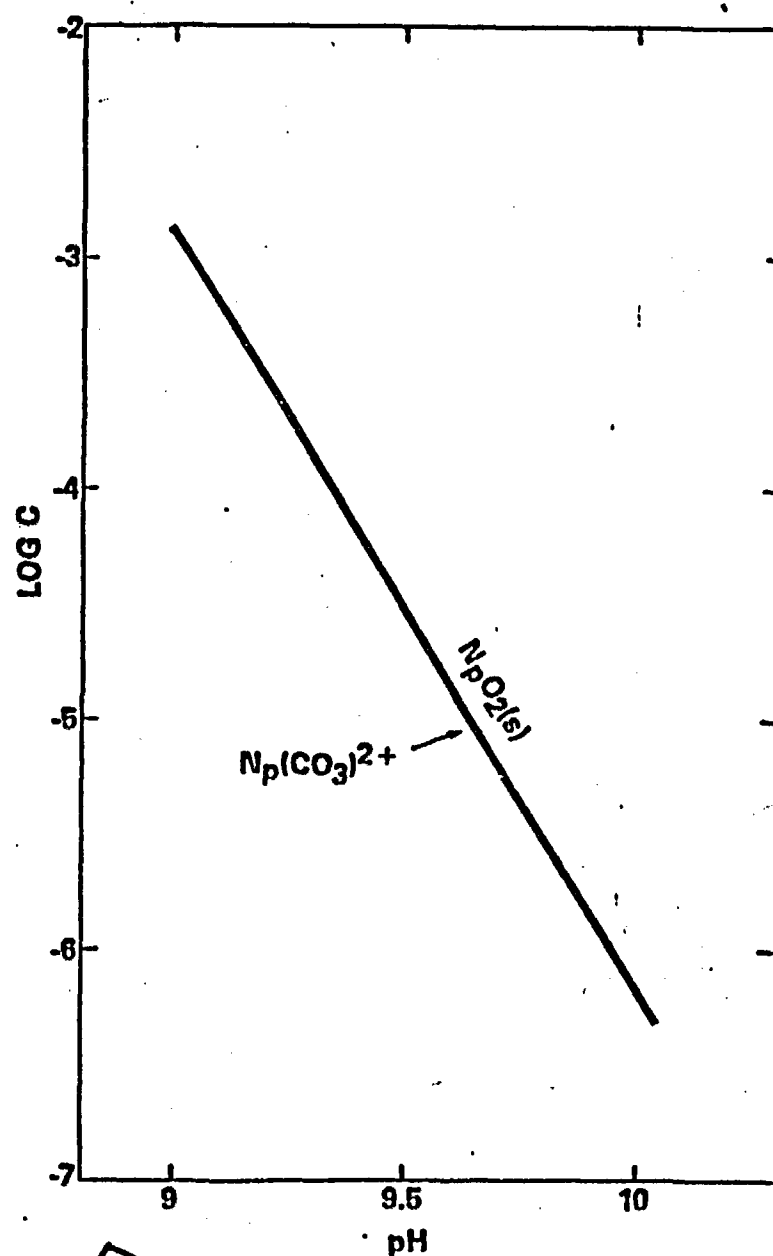


Figure 5b.

U-26

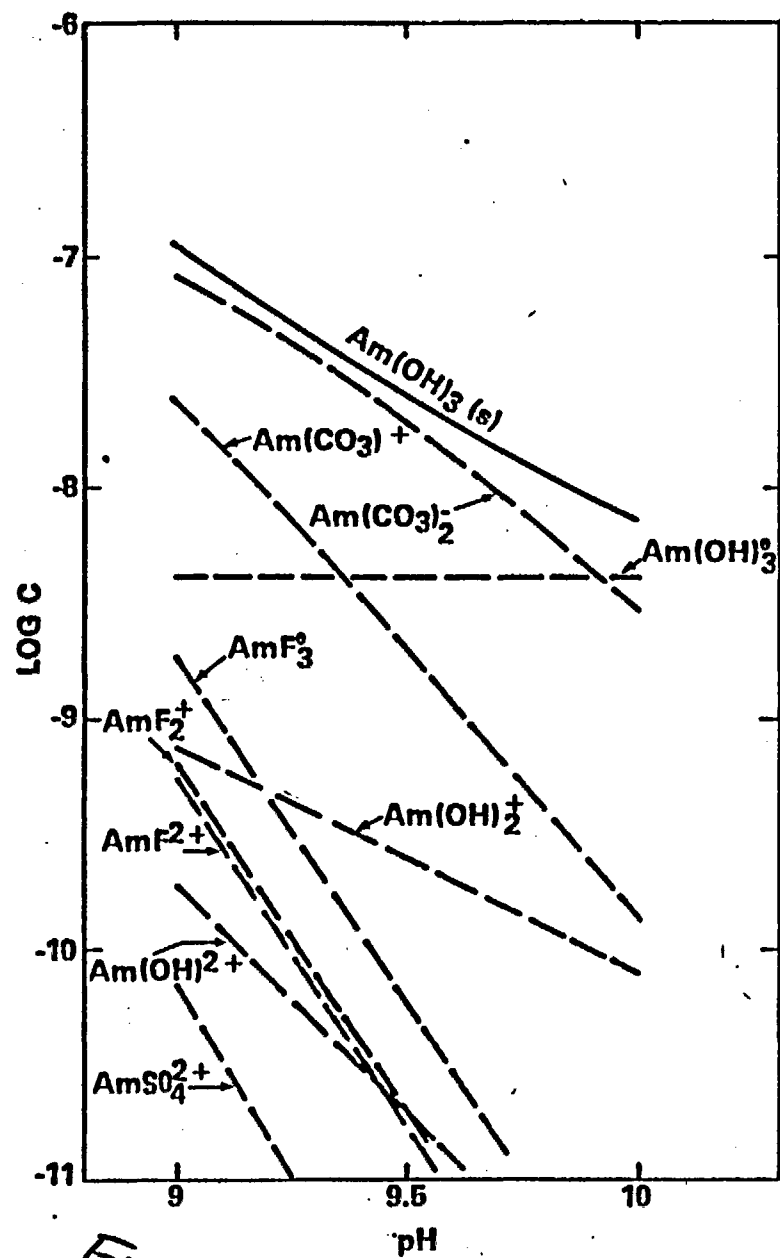


Figure 6a.

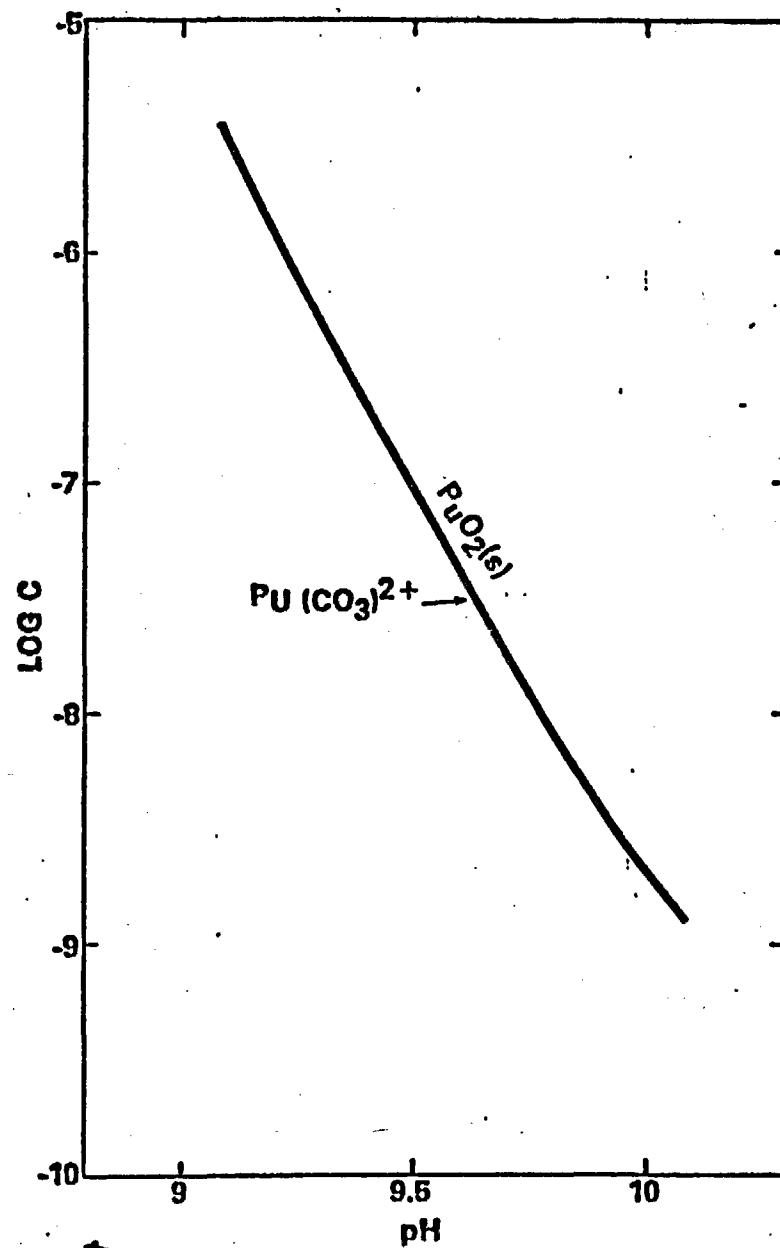


Figure 6b.

3.5 Additional Factors Which May Increase Actinide Solubilities

A number of additional factors must be considered before the maximum allowable concentrations of U, Np, Pu and Am in Hanford groundwaters can be established. Thermodynamic data for formation and hydrolysis constants for groundwater ligand-actinide complexes (organic and inorganic) and for the formation of potential polymers and colloids will be required. Thermodynamic data for estimating solubilities at anticipated near-field temperatures and high ionic strength will also be required since solubilities can change markedly due to changes in these parameters (Phillips and Silvester, 1982). Transients in near-field Eh-pH conditions will result from water-rock reactions at elevated temperatures and thus calculations of solubility limits will be required for a much broader range of pH and Eh than reported in our calculations or those in the SCR.

3.6 Conclusions

The conclusions on page 6.4-3 of the SCR that ~~"Based on solubility, the maximum permissible release rates will be below the NRC 10⁻⁵ proposed release criterion and EPA proposed cumulative release criteria"~~ are premature and inaccurate for the following reasons:

1. Thermodynamic estimates of the position of the univariant curves for the solubility limiting solid phase (e.g., $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{s})$, $\text{UO}_2(\text{s})$, $\text{NpO}_2(\text{s})$, $\text{Am}(\text{OH})_3(\text{s})$ and $\text{PuO}_2(\text{s})$ in Figures 4-6) require that the cumulative contributions by all important complexes are accounted for in the limit. Failure to account for all important complexes (e.g., carbonate complexes) will result in underestimates of the maximum concentrations that could be achieved under repository conditions. In addition to common inorganic anions typical of deep groundwaters (e.g., OH^- , HCO_3^- , CO_3^{2-} , HPO_4^{2-} , F^- , SO_4^{2-} , H_3SiO_4^- , $\text{H}_2\text{SiO}_4=$), anions that will be released by the waste package (e.g., H_2BO_4^- , HBO_4^- , BO_4^{3-}) must also be considered. Therefore, neither our analysis nor that presented in the SCR are complete.
2. Further, research will be required in order to resolve data discrepancies for $\text{AnO}_2(\text{s})$, $\text{An}(\text{OH})_3^-$, AnCO_3^{2+} [An = actinide] and $\text{UO}_2(\text{CO}_3)_6^{6-}$ which are important in the thermodynamic estimates.
3. The importance of organic complexes in Hanford groundwaters on actinide solubilities should be assessed since, if present, they could increase actinide solubilities.
4. The potential for the formation of actinide polymers and colloids in Hanford groundwaters should be assessed since they could increase actinide solubilities.
5. Potential increases in actinide solubilities resulting from near-field thermal effects or variability in Eh-pH along flowpaths should be assessed.

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→ "Based on solubility, the maximum possible release rates for all the radionuclides considered will be below the 10⁻⁵ proposed release criterion (NRC, 1971) and the draft cumulative release criterion (EPA, 1970)."

U-40 BWIP DSCA/APP U/CORRADO

4.0 SUMMARY AND CONCLUSION

The rate at which radionuclides are transported to the accessible environment will be determined by their solubilities (initial concentrations in groundwater), the rate and path of groundwater movement, and the retardation (both chemical and physical) of the radionuclides by minerals in the backfill and in fractures in the host rock.

Theoretical analyses of likely radionuclide solution species and solubilities (under anticipated reducing conditions) and low groundwater velocities suggest that their extremely low solubilities will limit their release to the accessible environment. However, the degree to which solubility will limit releases from a repository cannot be defined at this time. The determination of radionuclide aqueous speciation, radionuclide solubilities, and supporting thermodynamic data is a logical first step in assessing the importance of subsequent geochemical interactions for controlling radionuclide migration.

The basic elements of a program for determining radionuclide speciation and solubility limits include (1) groundwater characterization and (2) the determination of radionuclide solubilities. An adequate plan for characterization of groundwater includes technically acceptable methods for groundwater sampling, chemical analyses, redox couple measurements, data reduction, statistical analyses, and interpretation. Subsequent elements of a program for determining radionuclide speciation include describing reactions for speciation of radionuclides at appropriate valence states with available ligands and limiting the number of species that must be considered. A possible approach for this would involve the use of Eh-pH dominance diagram computer codes. The basic elements of a program for determining the solubilities of radionuclides consist of compilation of thermodynamic data for dominant species, assessment of solubility limits for dominant species, and laboratory validation of solubility-limit data (including technology for characterization of the solid phase, speciation of solid and solution phases, and analysis of the aqueous phase).

5.0 REFERENCES

1. Allard, B., 1982, "Solubilities of Actinides in Neutral or Basic Solutions," in Proceedings of the Actinides 1981 Conference: Oxford, Pergamon Press, 28 p.
2. Amphlett, C. B., 1964, Inorganic Ion Exchangers, Elsevier Publishing Co.
3. Arthur D. Little, Inc., 1977, Technical Support of Standards for High-Level Radionuclide Waste Management, vol., Source Term Characterization, EPA Report 520/4-79-007A.
4. Baes, C. F., Jr., and Mesmer, R. E., 1976, "The Hydrolysis of Cations," John Wiley & Sons, New York.
5. Benson, L. V., Carnahan, C. L., and Che, M., 1980, "A Study of Rock-Water-Nuclear Waste Interactions in the Pasco Basin, Washington, Part II: Preliminary Equilibrium - Step Simulations of Basalt Diagenesis: LBL-9677," Lawrence Berkeley Laboratory, Berkeley, CA.
6. Brown, R., Skoug Stad, M. W., and Fishman, M. J., 1970, "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," in Techniques of Water Resource Investigations of the U.S. Geological Survey, Book 5, Chapt. A-1, U.S. Geological Survey, Reston, VA.
7. Bucher, J., and N. Edelstein, 1982, "Hydrolysis and Solubilities of Cm(III), Nd(III) and Np(V)," ONWI Topical Report LBL-15056.
8. Burney, G. A., and Harbour, R. M., 1974, Radiochemistry of Neptunium, National Academy of Sciences, National Research Council, NAS-NS-3060, U.S. Tech. Info. Service, U.S. Department of Commerce, Springfield, VA, p. 23.
9. Cleveland, J. M., T. F. Rees, and K. L. Nash, 1982, "Chemical Speciation of Plutonium in Selected Ground Waters." 183rd American Chemical Society National Meeting, Las Vegas, [Abstract].
10. Deutsch, W. J., Jenne, E. A., and Krupka, K. M., 1981, "Solubility Equilibria in Basalt Aquifers: The Columbia Plateau, Eastern Washington," Draft PNL Report, 30 pp.
11. Edelstein, N., J. Bucher, R. Silva, and H. Nitsche, 1983, "Thermodynamic Properties of Chemical Species in Nuclear Waste. ONWI-399, Columbus, Ohio.
12. Ellis, A. J., Mahon, W. A. J., and Richie, J. A., 1968, "Methods of Collection and Analysis of Geothermal Fluids," 2nd Ed. Chem. Div. Dept. of Scientific and Industrial Res., New Zealand, Report No. CD 2103, 51 pp.
13. EPA, 1982, Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes. Federal Register, Vol. 47, No. 250, Proposed Rules, pp. 58196-58204.

14. Feitknecht, W. and Schindler, P., 1963, "Solubility Constants of Metal Oxides, Metal Hydroxides and Metal Hydroxide Salts in Aqueous Solution," Pure and Applied Chemistry, 6, p. 130-199.
15. Ferri, D., I. Grenthe, and F. Slavatore, 1981, "Dioxouranium (VI) carbonate complexes in neutral and alkaline solutions," Acta Chem. Scand. Vol. A 35, 165-168.
16. Fuger, J. and Oetting, F. L., 1976, The Chemical Thermodynamics of Actinide Elements and Compounds--Part 2--the Actinide Aqueous Ions, I.A.E.A., Vienna, 65 pp.
17. Garrels, R. M., and C. L. Christ, 1965, Solutions, Minerals and Equilibria, Harper & Row, New York, 450 pp.
18. Grenthe, I. and D. Ferri, 1981, "Actinide Species in Groundwater Systems." Proc. OECD/NEA Workshop on Near-Field Phenomena in Geologic Repositories for Radioactive Waste, Seattle, in Press.
19. Haire, R. G., Llyod, M. H., Beasley, M. L., and Milligan, W. O., 1971, "Aging of Hydrous Plutonium Dioxide," Journal of Electron Microscopy, 20, 8-16.
20. Haire, R. G., Lloyd, M. H. Milligan, W. O., and Beasley, M. L., 1977, "Lattice Parameters of $^{244}\text{Cm}(\text{OH})_3$ and the Effect of Self-Irradiation on Crystalline $^{241}\text{Am}(\text{OH})_3$ and $^{244}\text{Cm}(\text{OH})_3$," J. Inorganic and Nuclear Chemistry, 39, 843-847.
21. Kraus, K. A., Phillips, H. O., Carlson, T. A., and Johnson, J. S., Jr., 1958, "Ion Exchanges Properties of Hydrous Oxides," Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Vol. 28, 3-16.
22. Langmuir, D., 1971, "Eh-pH Determinations," Procedures in Sed. Pet., R. W. Carnen, ed., Chapt. 26, John Wiley and Sons, New York, pp. 597-634.
23. Lemire, R. S. and Tremaine, P. R., 1980, "Uranium and Plutonium Equilibria in Aqueous Solutions to 200°C," Chem. Eng. Data, Vol. 25, pp. 361-370.
24. Lohdquist, R., 1982, "Hydrophilic Complexes of the Activities: I. Carbonates of Am and Eu," Accepted for publication in Acta Chemica Scandinavica.
25. Moody, J. B., 1982, "Radionuclide Migration/Retardation: Research and Development Technology Status Report," ONWI-321, Office of Nuclear Waste Isolation, Columbus, Ohio.
26. Morris, J. C., and Stumm, W., 1967, "Redox Equilibrium and Measurements of Potentials in the Quatic Environment, Equilibrium Concepts in Natural Water Systems," Advan. Chem. Series, 67, p. 270-285.

21. Nitsche, H. and Edelstein, N., 1982, "Carbonate Complexation of Np(v) in Near Neutral and Basic Solutions," ONWI Topical Report LBL-14935.
22. Phillips, S. L., 1982, "Hydrolysis and Formation Constants at 25°C," LBL-____, Presented in part, 183rd National ACS meeting, Las Vegas, NV, March 26-April 2, 1982.
23. Phillips, S. L., and L. F. Silvester, 1982, "A data Base for Nuclear Waste Disposal for Temperatures up to 300°C," LBL-14722, Lawrence Berkeley Laboratory, Berkeley, California.
24. Pinta, M., 1978, "Modern Methods for Trace Element Analysis," Ann Arbor Science, Ann Arbor, MI, 492 pp.
25. Polansky, P. and Baer, J., 1977, "Ultrafiltration of Solution of Y Tritium in Trace Concentrations," Collection Czechoslov. Chem. Commun., 42, pp. 1299-1303.
26. Rai, D., and Serne, R. J., 1978, "Solid Phases and Solution Species of Different Elements in Geologic Environments," PNL-2651, 129 pp.
27. Rai, D., and Serne, R. J., and Swanson, J. L., 1980, "Solution Species of Plutonium in the Environment," in J. Environ. Qual., Vol. 9, no. 3, pp. 417-420.
28. Rai, D., Serne and D. A. Moore, 1980, "Solubility of Plutonium Compounds and their Behavior in Soils. Soil Sci. Soc. of America J., 44, 490-495.
29. Rai, D., Strickert, R. G., Moore, D. A., and Serne, R. J., 1981, "Influence of an Americium Solid Phase on Americium Concentrations in Solutions," in Geochim. et Cosmochim. Acta Vol. 45, pp. 2257-2265.
30. Shade, J. W. and Bradley, D. J., 1980, "Initial Waste Package Interaction Tests: Status Report," Pacific Northwest Laboratory Report PNL-03559.
31. Silva, R. J., 1982, "Solubilities of Crystalline and Am Trihydroxides," ONWI Topical Report LBL-15055.
32. Silva, R. J., and A. W. Yec, 1982, "Uranium (vi) Retardation Mechanisms," Earth Science Division Annual Report 1981, LBL-13600, pp. 45-47.
33. Stumm, W., 1966, "Redox Potential as an Environmental Parameter; Concepted Significance and Operational Limitation," 3rd Int. Conf. on Water Pollution Research, Sec. 1, No. 13, Water Pollution Control Federation, Washington, DC, p. 1-16.
34. Thorstenson, D. C., 1982, "The Concept of Electron Activity and the Redox Potential of Aqueous Solutions," ACS/Division of Nuclear Chemistry and Technology.

- 41 33. Thorstenson, D. C., and Fisher D. W., 1979, "The Geochemistry of the Fox Hills - Basal Hill Creek Aquifer in Southern North Dakota and Northwestern South Dakota," Water Resources Research, Vol. 15, No. 6, pp. 1479-1498.
- 42 34. Winefordner, J. D., 1976, "Trace Analysis, Spectroscopic Methods for Elements," Vol. 46, John Wiley and Sons, New York, 484 pp.
- 43 35. Wood, B. J., and Rai, D., 1980, "Nuclear Waste Isolation: Actinide Containment in Geologic Repositories," PNL Draft Report, 31 pp.
- 44 36. Wood, B. J., and Rai, D., 1981, "Nuclear Waste Disposal: Actinide Migration from Geologic Repositories," Battelle Pacific Northwest Lab. Rept. PNL-SA-9549, 33p.
- 45 37. Wood, M. I., 1980, "Groundwater Geochemistry and Interaction With Basalt at Hanford," ONWI-212, Office of Nuclear Waste Isolation, Columbus, OH.
- 46 38. Wood, W. W., 1976, "Guidelines for Collection and Field Analysis of Groundwater Samples for Selected Unstable Constituents," Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 2, U.S. Geological Survey, Reston, VA.
- 47 39. Zimmerman, H. K. Jr., 1952, "The Experimental Determination of Solubilities," Chemistry Revision 51, pp. 25-65.

APPENDIX V
DESIGN OF ~~STABLE~~ OPENINGS
REPOSITORY

1 INTRODUCTION

The objectives of constructing a nuclear waste repository are to terminally store the waste and isolate the radionuclides from the biosphere. In an effort to verify the performance of the repository and ensure that its objectives are fulfilled, the proposed 10 CFR 60 rules specify a retrievability period of 50 years from the initiation of waste emplacement. There are several openings in a repository and the stability of these openings must be maintained, at least during the retrievability period. The design of stable shafts, main access drifts, waste emplacement rooms and holes is a major consideration in the repository design.

The Nuclear Regulatory Commission (NRC) has proposed a set of rules in 10 CFR 60 which will provide a framework for licensing nuclear waste repositories. 10 CFR 60.132 provides the design requirements for the underground facility. 10 CFR 60.141 provides the guidelines for the confirmation of geotechnical and design parameters during repository construction and operation. In this appendix, a design logic is presented which will assist in compliance with the requirements in 10 CFR 60.132. A phased approach to design is described which will assist in compliance with the requirements in 10 CFR 60.132. A phased approach to design is described which will permit the use of data obtained from the surface to develop a conceptual design, and refine the design as in situ data is obtained from test excavations in the repository horizon.

The applicability of the design approach to the Basalt Waste Isolation Project (BWIP) is briefly discussed, and areas of concern in the conceptual design presented in the BWIP Site Characterization Report (SCR) are described.

2 DESIGN LOGIC FOR NUCLEAR WASTE REPOSITORIES

A sound design philosophy, for any opening requiring long-term stability in rock, follows a pattern in which greater accuracy and detail is obtained as additional information becomes available. The design is complete when it fully addresses all geological conditions that may impact the stability of the opening under the conditions and nature of its use.

2.1 A Phased Approach to Design

Engineering for underground openings begins with assessments of the properties of the medium to be used in construction--the naturally occurring rock mass. The engineering properties of the rock mass are never known accurately and have to be estimated. They are expressed in terms of probabilities that the estimates agree with actual geological conditions as they are distributed in the ground.

The accuracy of geological assessments, and therefore, the efficiency and reliability of design concepts based on them, is the lowest at early phases of exploration and increases as progress is made in exploration and construction. Modern rock engineering practice recognizes that although the accuracy of geological predictions must be improved as the exploration effort progresses,

the scope of those same predictions must at all stages include the range of factors expected to impact the performance of the opening, i.e., rock mass mechanical properties, in situ stress, and hydrogeology.

Certain factors influence the performance of rock masses for all openings, regardless of the nature of the geologic medium or the purpose of the opening. These include the distribution of rock mass strengths, the stress field, and hydrogeologic setting. Methods exist for assessing these complex and spatially variable characteristics. In arriving at a preliminary design such methods are comprehensive, but must be carefully utilized to cover specific project requirements.

Basic rock engineering principles and specific project requirements should be incorporated into preliminary design concepts using methodology appropriate to the accuracy of the data at hand. Early in the project, geologic data are obtained remotely, and are regarded as somewhat speculative. Conceptual designs are, therefore, generalized and tend to be conservative. As further data are gained, a more accurate description of the rock mass is obtained. At these early stages, empirical design approaches are appropriate. They enable preliminary design concepts to be evaluated and compared.

Subsurface exploration by drilling and later firsthand examination of the rock from test drifts, shafts, or rooms affords a level of detail that justifies closed-form or numerical analysis. The resulting design may still be conservative, but a better estimate of the degree of conservatism is obtained. Depending on the project, specialized, in situ tests may be required to address specific design requirements in detail.

Current methodology for a comprehensive design approach with preliminary or generalized geologic data incorporates empirical rock classification systems. The recommendations, thus generated, can be modified to allow for specific concerns. For a nuclear waste repository, such concerns relate to thermal loading, the need for stability during the retrieval period, and the need for long-term isolation of radionuclides.

A comprehensive design approach based on more detailed geologic data may incorporate analytical or numerical modeling techniques. Analytical techniques commonly require some simplification and generalization of site conditions. While some detail is necessary in the data, a high level of detail is inappropriate. Numerical modeling techniques require a well-defined data base consisting of reliable geologic data and workable underground layout concepts. The proper use of empirical and analytical techniques during the earlier design stages may limit the number of alternatives considered during numerical analysis, with consequent savings in time, effort, and cost.

The following sections will introduce this phased approach and outline some accepted methods for carrying out the strategy. For the case of a nuclear waste repository, the strategy should enable the numerous repository design concepts to be compared in light of a full range of geologic factors.

2.2 Critical Design Input Parameters

Design input parameters that govern or constrain repository planning must include geological/hydrological considerations and parameters relating to repository layout and use. Geological/hydrological considerations relate to the basic fact that a geological repository is an underground structure excavated in rock which is governed by rock mass characteristics. Design considerations also depend on repository layout and use, and extend to thermal loading, the retrievability criteria, repository life, isolation of radionuclides, operational factors such as rate of emplacement of and capacity for nuclear waste, and safety. These factors dictate the repository layout and support facilities, and hence, govern the selection of design criteria and specifications.

Geologic factors that should be addressed at all stages of the design process are as follows:

- (1) Rock strength is one of the several factors controlling the deformation of the rock surrounding the opening, and needs to be assessed in terms of shear, tension, compression, time, and temperature.
- (2) Rock fracturing also contributes to rock deformation. Where the intact rock strength is high compared to the stresses to be imposed, rock fracturing may be a determinant of rock mass behavior. Important aspects are the orientations of the fractures (with respect to the opening), their inherent shear strength, continuity, extent, and spacing. Laboratory testing should determine the shear strength of the full range of fracturing conditions, both wet and dry.
- (3) In situ stresses affect the location and magnitude of stress concentrations around the opening, and the mode of rock mass deformation that must be designed for. Opening shape and orientation, and rock reinforcement pattern, will depend in large part on the stress field. Some fractures will be more favorably oriented than others. Opening shapes and orientations tending to cause very high compressive stresses or large tensile areas in the crown should be avoided. The stress field is, therefore, important even in preliminary design and early assessments should be obtained. The hydrofracturing technique is suitable for measuring in situ stresses at depth; however, interpretations of test results should consider the limitations of the technique. Over-coring and other stress relief techniques are desirable when greater accuracy is required in later site characterization efforts, but the data reduction and procedures selected should be adaptable to fractured rock.
- (4) Elastic properties of the rock and fractured rock mass are required for numerical modeling and some analytical design techniques. The laboratory Young's Modulus and Poisson's ratio from compression and sonic velocity tests are required to compute deformability of intact rock blocks and theoretical stress distributions. Rock mass elastic properties can be estimated through seismic geophysical testing (yielding a "dynamic" modulus) or in situ jacking tests that yield a modulus of deformation from which the static elastic rock mass

properties can be obtained through back-calculation. Borehole geophysical testing, which for many rock masses yields a higher modulus value than static jacking tests, is nonetheless a rock mass value and can be obtained early in the design effort. The effect of natural discontinuities can be conceptualized through comparison of seismic dynamic modulus and laboratory sonic modulus.

- (5) Thermal response of the rock mass must be determined to ensure that the heat generated by the emplaced waste does not threaten the long-term integrity of the structure. A data base on the properties of the rock at elevated temperatures is needed, to determine the coefficient of linear thermal expansion, thermal conductivity, and specific heat of the rock mass.

Heater tests are required to determine the thermal response of the rock mass. These can be conducted after test excavations have been completed in the horizon of interest. The data can then be utilized to refine the preliminary design.

- (6) The Hydrogeologic regime affects the stability of the opening and poses a potential pathway for radionuclide migration. The presence of groundwater creates an internal pressure that must be overcome by the support system, weakens potential failure surfaces, and complicates construction operations. Testing should determine the hydraulic conductivities and storage coefficients at the repository horizon, hydraulic gradient, the hydraulic head, and whether constituents are present that could be damaging to the support system (steel and grout).
- (7) A definition of instability is necessary so that conformance of the rock behavior with stability criteria can be verified. This definition provides a framework for design by establishing the extent of deformation or localized failure that can be tolerated in the repository.
- (8) The expected performance of rock support systems needs to be established prior to inclusion of such systems in the repository design. Principal concerns relate to temperature effects and creep.

2.3 Design Approaches

The design of stable openings, as discussed earlier, is a phased process in which the conceptual design is refined as more data become available from in situ testing. The sequence begins with empirical, general concepts, which allow selection of several suitable options for further study. Information needs are identified, data are collected accordingly, and designs based on engineering mechanics are carried out (analytical techniques). A comparison of the designs is then possible, perhaps based on cost and technical criteria. A few alternatives are then selected for detailed consideration, in which the interaction of all critical design factors is evaluated through numerical modeling; this design phase should be supported by in situ testing for specific input parameters. From this effort, design specifications and performance criteria are formulated. Finally, the conformance of the rock mass behavior with performance criteria is established by monitoring.

2.3.1 Engineering Mechanics

Design approaches based on engineering mechanics considerations are the rock classification schemes, and analytical solutions to analyze stability. Rock classification systems address most of the factors governing the stability of underground openings in rock, i.e., basic rock strength, fracturing, water conditions, and overall geologic setting. The RMSD method proposed by Kendorski (1980) is basically a discounting method in which the intact rock strength is discounted according to the nature and degree of fracturing to obtain the rock mass strength. This value can be used for analytical computations as well as an indicator of overall rock mass competence. The Geomechanics System of Bieniawski (1979) develops a relationship of span versus stand-up time. The Q-System of Barton, Lien, and Lunde (1974) is fairly simple, but is not recommended for the design of shotcrete and rock reinforcement. The system proposed by Terzaghi (1946) computes a dead rock load due to loosening, and is widely used for the design of steel arch support in tunnels.

These systems either enable or directly yield generalized support recommendations. Application of these systems to circumstances outside the classification data base requires discretion by the user. Thus, the particular requirements of nuclear waste repositories, especially thermomechanical effects, will require some modification of the direct results obtained from classification systems before an adequate preliminary design is obtained for any single repository concept. However, various repository concepts can be readily compared for long-term stability and constructibility using classification approaches. Typically, recommendations from the various classification systems are compared to obtain preliminary rock mechanics design concepts.

Classical engineering mechanics approaches are based on arriving at a balance of forces acting on an opening. Driving forces are the rock loads, and resisting forces come from the rock mass competence and the support system. The in situ material properties of the rock and support must be known for such an approach to be meaningful.

Simple elastic theory (Obert and Duvall, 1967) gives a first approximation of the distribution and magnitude of stresses and distressed zones surrounding an opening. However, the assumptions of homogeneity, isotropism, and linear elasticity implicit in elastic theory are seldom met in rock masses. Elastic theory also does not allow for the effects of rock reinforcement. However, even with these limitations, simple elastic analyses yield useful, though conservative, information for conceptual design of structures in rock.

Elastic-plastic ground reaction curve methods seek to match the support to the rock mass such that the amount of deformation allowed for corresponds both to the peak rock mass shear strength and the peak deformation resistance of the support (Egger, 1980). For the optimum use of the method, proper timing of support installation is essential. While the deformation of the support can be fairly readily evaluated, it is seldom possible to predict the ground characteristic from basic geomechanics data. Field measurements of rock mass behavior are necessary, and preliminary estimates can be obtained from underground test facilities within the horizon of interest. During construction, detailed geologic studies coupled with field measurements in the rock mass of

interest, can result in enhanced capability for predicting the ground characteristic in virgin ground.

2.3.2 Numerical Modeling

There are a variety of numerical modeling approaches available for use in the design of stable underground openings (St. John and Hardy, 1982). For a geologic repository, modeling appears at present to be the best way to address the following specific design issues.

- (1) Rock mass deformation around openings
- (2) Time-dependent behavior
- (3) Effect of hydrologic regime
- (4) Deviations from simple rock mass behavior due to thermal effects
- (5) Repository layout
- (6) Geologic variations: stress field, rock mass competence, and water conditions

The proper use of numerical modeling schemes requires a considerable base of reliable, in situ data as well as remotely-gained data. Hence, these methods are most useful when such data are available from underground test excavations. Also, some codes are quite complex and costly to use, and their use should be limited to the most favorable repository scenarios.

The U.S. National Committee on Rock Mechanics (1981) has summarized recent modeling schemes. These require the following types of data.

- (1) Geometry of opening and rock mass discontinuities
- (2) Heat transfer and fluid flow parameters
- (3) Assumptions of finite or infinite strain
- (4) Nature and properties of the rock mass and its mode of deformation
- (5) In situ stress
- (6) Excavation methods
- (7) Support-rock interaction

Computer modeling schemes fall into the two categories of differential methods and integral methods. Desai and Christian (1977) discuss the theory behind numerical modeling schemes.

Differential methods (finite element and finite difference) permit the introduction of interfaces (slide lines or element boundaries) within a continuum. The finite element method (FEM) (Zienkiewicz, 1971) has the advantages of handling complex geometries, inhomogeneities, nonlinearity, and support-rock interaction. In problems involving repository excavations, several nonlinear phenomena may need to be considered. These involve plasticity, creep, nonlinear behavior of joints, and other complex constitutive relations including coupled thermal-mechanical response of rock mass.

Elastic-plastic methods hold significant potential in their ability to model the complexities of repository design concepts, and the ability to handle inhomogeneities. One important aspect of the elastic-plastic model in the definition of a damaged zone in the rock where yielding has propagated, away from the opening and into the rock mass, according to the selected yield

criterion (Goodman, 1980). Certain associated aspects of the conceptual elastic-plastic model, which need to be considered in applications to design of repository openings are: the change in both stiffness and strength of the damaged rock, the influence of time (and distance from the face) before installation of supports, and the support-rock interaction.

Integral or boundary-element methods are based on the solution of integral equations that connect the boundary tractions to boundary displacements (Crouch, 1976; Cruse and Rizzo, 1975). The boundary of the opening is discretized and defines the solution for the interior. Thus, these methods are most applicable when conditions at the boundary are of most concern.

Thermomechanical behavior can be modeled by the principle of superposition, in which stresses due to thermal and excavation effects are added. Thermomechanical modeling develops thermal stress values for this purpose; an example is ADINA/ADINAT (Bathe, 1978) which has been used to model the repository environment. Two-dimensional models can be useful for preliminary design. Coupled models assess the interaction of thermomechanical and hydrological conditions. Three-dimensional models avoid the simplifying assumptions inherent in a two-dimensional approach, but are more complex and costly. They do, however, allow for anisotropic rock behavior.

2.3.3 Observations During Construction

During the construction of any underground facility, in situ monitoring of the rock mass is essential for verification that design objectives are being achieved.

In conformance with the provisions of 10 CFR 60.141 and 60.142, a full monitoring program should be implemented. This should include measurements of relative and absolute ground movements, support load response, visual performance of support, geologic mapping, hydrologic monitoring, and records maintenance. Specific plans will depend on the design of the repository, but should be complete and at a level of accuracy that affords prediction of rock mass behavior.

Analysis of these data may lead to redesign of some construction elements. Since prediction of geologic conditions is not an exact science, some redesign is anticipated in even the most thoroughly investigated underground construction projects.

The process of design based on instrumentation and construction monitoring is the basis of the New Austrian Tunneling Method (NATM). The NATM is widely accepted in Europe and requires a high degree of interaction between the construction contractor and the owner/designer. Elements of the NATM approach may be suitable for repository construction, and should be carefully considered.

3 APPLICABILITY OF THE DESIGN APPROACH

The design logic presented in Section 2 can be applied successfully to a jointed rock such as basalt. The data collected to date at the Hanford site can be analyzed to provide the following design input parameters:

- Rock mass strength and elastic properties
- In situ stress magnitude and direction
- Groundwater pressure and flow
- Rock mass thermal properties

These parameters would be estimates obtained on the basis of laboratory test results scaled down to in situ values using geological, hydrological, and geomechanical data resulting from core logging, pump testing, and Near Surface Test Facility (NSTF) testing. The geomechanics classification systems mentioned in Section 2 can be used in estimating rock mass strength.

The excavation induced stresses can be obtained using analytical approaches and the 2-D numerical modeling method mentioned in Section 2. The loosened zone around the opening can be included in the 2-D numerical model by assuming a lower modulus value than the rock mass. Thermally induced stresses can be computed using the thermomechanical analyses mentioned in Section 2. The principle of superposition can be used to superimpose the thermal stresses on the excavation induced stresses. Stresses around the openings can be compared to the rock mass strength estimates to determine the stability of the openings. Deformation resulting from the stresses can be determined using the finite element technique.

The conceptual design obtained by the above mentioned techniques should have sufficient flexibility to accommodate the improvements that can be incorporated by using in situ data from the exploratory shaft testing. The estimates that were used for the design input parameters can be verified and/or refined as in situ data on rock mass strength, modulus of deformation, rock mass thermal properties, in situ stresses, and groundwater is obtained from the underground testing program. The spatial variability of the in situ data in the repository horizon can be estimated, and sensitivity analyses carried out using a range of expected design input parameters. These analyses will determine the effect of geologic variability on repository design.

The support system behavior under the expected temperature and moisture conditions should be analyzed using the data from in-situ monitoring in the underground test excavations. Design refinements can be constantly made as the data base from underground observations accumulates and provides greater confidence in the predictability of rock mass behavior.

4 AREAS OF CONCERN

There are several areas of concern in the BWIP Site Characterization Report (SCR) that have to be addressed in future SCR updates. These are related to in-situ stresses, rock mass strength, rock mass deformation, and repository design.

4.1 In-situ Stress

The in-situ stress measurements by the hydraulic freaturing method have to be verified by conducting overcoring (or other stress relief techniques) tests at

the bottom of the exploratory shaft. The spatial variability of in-situ stresses in the reference repository location (RRL) has to be established by conducting hydraulic fracturing tests in other boreholes in the RRL. The constructability of openings, both waste emplacement rooms and holes, in the high horizontal stress field should be established in the exploratory shaft testing program. Monitoring of deformation of the underground openings as they are excavated will provide an indication of the global rock mass stress conditions. The effect of the uncertainties in the assessment of the in-situ stress field on repository design should be evaluated.

4.2 Rock Mass Strength

Rock mass strength should be estimated on the basis of geological data collected to date, data from the NSTF, and laboratory test results. Estimates arrived at independently by the NRC using the BWIP laboratory data and core log information indicate that the rock mass strength may be about one-half of the 200 MPa used in the BWIP conceptual design. Rock mass strength should be determined using the heated block test, and other appropriate tests in the exploratory shaft bottom. Detailed mapping of underground exposures should be done, especially in the areas where rock mass strength tests are to be conducted. This will permit correlation of mass strength with the discontinuity characteristics of the rock. Derived correlations can then be used to predict the rock mass strength throughout the repository. Rock mass strength assessment should include the effect of moisture (various degrees of saturation), temperature and time.

4.3 Rock Mass Deformation

Rock Mass deformation modulus should be measured in the bottom of the exploratory shaft by conducting the Rocha Slot test or other appropriate tests. In addition, monitoring of all underground drifts will provide an estimate of rock mass deformation and support requirements in the repository. Deformation should be carefully measured in heater tests to determine the effect of temperature increase on rock mass deformation. In essence, the rock mass constitutive relationship under expected repository conditions should be established.

4.4 Repository Design

The waste emplacement rooms have been designed as ovaloids to accommodate the high horizontal stress; however, the reaming rooms are designed in a horseshoe shape. This might cause overstressing and instability. The sensitivity of the various input parameters, especially rock mass strength and modulus, thermal properties, and geologic structure, have not been considered in the design. Sensitivity analyses are important because they provide valuable guidance in data gathering efforts at the bottom of the exploratory shaft.

The effects of moisture, temperature and time on the performance of the support system have not been fully considered. These effects and the effect of thermal loading on the stability of waste emplacement holes are major factors in providing for local retrieval from portions of the repository which are deemed unsuitable from a geologic standpoint.

The basis for orientation of the rooms and waste emplacement holes seems to be the in-situ stress field; however, the effect of groundwater flow seems to have been neglected. The justification for selecting the maximum design stress and the maximum design temperature is not clear and seems to be based on laboratory derived values. The manner in which the conceptual design will be changed to accommodate the geologic, geohydrologic, and geomechanics data obtained from the exploratory shaft testing program is not described in the SCR. In addition, the effect of geologic variability within the repository horizon on repository design is not discussed.

5 CLOSURE

A design logic for stable openings is presented in this appendix which can accommodate the improving nature of the data base inherent in geologic exploration. The need for flexibility in the conceptual design is emphasized since this will allow for design improvements based on in-situ data to be obtained from the exploratory shaft. A phased design approach, which is applicable to a fractured hard rock such as basalt, is presented. Critical design input parameters are discussed since they define the information needs for resolving several issues affecting repository design.

The applicability of the design approach to the BWIP subsurface design is discussed. Several techniques are available to satisfy this design approach, the key elements of which are the determination of rock mass characteristics and the stresses and deformations resulting from excavation and thermal loading. The importance of monitoring subsurface openings and using the monitored data to improve the design are emphasized.

Areas of concern in the conceptual design presented in the BWIP Site Characterization Report are briefly discussed. Ongoing site characterization and design efforts could resolve these areas of concern.

REFERENCES

1. Barton, N., Lien, R., and Lunde, J., 1974, "Engineering Classification of Rock Masses for the Design of Tunnel Support," Jour. Ont'l. Soc. Roc Mech., Vol. 6, No. 4, pp. 189-236.
2. Bathe, K., 1978, "ADINA - A Finite Element Program for Automatic Dynamic Incremental Nonlinear Analysis," MIT Report 82448-1, Cambridge, Massachusetts.
3. Bieniawski, Z. T., 1979, "The Geomechanics Classification in Rock Engineering Applications," Proceedings, 4th International Congress on Rock Mechanics, ISRM, Montreaux, Switzerland.
4. Crouch, S. L., 1976, "Analysis of Stresses and Displacements Around Underground Excavations" an Application of the Displacement Discontinuity Method," Geomechanics Report, University of Minnesota.
5. Cruse, T. A., and Rizzo, F. J., 1975, "Boundary Integral Equation Method," Computational Applications in Applied Mechanics, Am. Soc. Mech. Engr., New York.
6. Desai, C. S., and Christian, J. T., 1977, "Numerical Methods in Geotechnical Engineering," McGraw-Hill, London 783 p.
7. Egger, P., 1980, "Deformations at the Face of the Heading and the Determination of the Cohesion of the Rock Mass," Underground Space, Vol. 4, No. 5, pp. 313-318.
8. Goodman, R. E., 1980, "Introduction to Rock Mechanics," John Wiley & Sons, New York.
9. Kendorski, F. S., 1980, "Field and Laboratory Assessment of Rock Mass Strength for Tunnel Design with Allowance of Dilation." Proc. 13th Can. Rock MECh. Symp., Underground Rock Engineering, Special Vol. 22, CIM, Montreal, pp. 162-167.
10. Obert, L., and Duvall, W., 1967, "Rock Mechanics and the Design of Structures in Rock, Wiley, New York.
11. St. John, C. M., and Hardy, M. P., 1982, "Geotechnical Models and their Application in Mine Design," pp. 1479-1488 in Hustrulid, W. A., ed., Underground Mining Methods Handbook, Soc. Min. Engr. AIME, New York, 1754 p.
12. Terzaghi, K., 1946, "Rock Defects and Loads on Tunnel Supports," in R. V. Proctor and T. L. White, Rock Tunneling with Steel Supports, Commercial Shearig and Stamping Co., Youngstown, Ohio.

13. Wickham, G. E., and Tiedemann, H. R., 1974, "Ground Support Prediction Model-RSR Concept," Final Report on USBM Contract H0220075, January.
14. Zienkiewicz, O. C., 1971, "The Finite Element Method in Engineering Science," McGraw-Hill, London.

FINAL DRAFT

**APPENDIX W
RELEASE RATE FROM THE ENGINEERED SYSTEM**

**Prepared by
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1 INTRODUCTION

A geologic repository for long-term disposal of nuclear waste materials is comprised of an engineered facility located at depth in a stable, well characterized geologic environment. Isolation of the wastes from the biosphere is to be achieved by a combination of long radionuclide transport time through the geologic media backed by an engineered design having a predictable radionuclide containment time and release rate from the engineered system.

The purpose of this Appendix is to examine the intent of the radionuclide release criteria as defined in the current NRC/EPA regulations, how release rates are determined, and the current uncertainties associated with that determination for the Hanford site. The specific regulatory requirements are summarized in Section 2. Definitions of the engineered system and components are outlined in Section 3. The determination of release rates, including performance criteria, data and modeling requirements are presented in Section 4. Areas of concern for the Hanford site, based on existing studies, are discussed in Section 5.

2 REGULATORY REQUIREMENTS

2.1 Performance Objectives

The overriding performance objective [60.111(b)(1)] for a repository is to meet the EPA criteria proposed in draft 40 CFR Part 191 (Draft 21). The criteria specified by the EPA are in terms of a maximum cumulative release to the accessible environment, for each radionuclide, for a period 10,000 years after disposal. For release involving more than one radionuclide, the allowed release for each radionuclide is reduced to the fraction of its limit that insures that the overall limit is not exceeded. Cumulative release limit criteria for high-level waste are specified in Table 2-1.

The EPA defines accessible environment to include the atmosphere, land surfaces, surface water, oceans, and parts of the lithosphere that are more than 10 kilometers in any direction from the original location of the radioactive wastes in a disposal system. The NRC has recognized that there are large uncertainties involved in predicting radionuclide transport processes through the portion of the geologic setting that is significantly affected by construction of the subsurface facility, or by the heat generated by the emplacement of radioactive waste. The proposed NRC technical Rule 10 CFR Part 60 includes specific performance objectives for two parts of the engineered system, the waste package and the underground facility, in addition to a criteria for pre-waste emplacement groundwater travel time through the far field to the accessible environment.

In addition, there are specific regulatory requirements for the development of engineered barriers, which can be grouped into four areas:

- (1) Engineered system design requirements
- (2) Analysis of the performance of the engineered system
- (3) Verification of data and models used in analysis
- (4) Confirmation of engineered system performance

TABLE 2-1

CUMULATIVE RELEASES TO THE ACCESSIBLE
ENVIRONMENT FOR 10,000 YEARS AFTER DISPOSAL^(b)

Radionuclide	Release Limit ^(a) (curies per 1000 MTHM)
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

*Limiting values for a mixture of radionuclides

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 , and RL_c , then the cumulative releases over 10,000 years should be limited so that:

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

- (a) The release limits also apply to each unit of transuranic wastes containing three million curies of alpha-emitting transuranic nuclides.
- (b) These release limits shall be met for all anticipated processes and events, defined as those estimated to occur with a frequency of 0.01 or more over 10,000 years. For very unlikely events, those with a frequency of occurrence of between 10^{-2} and 10^{-5} over 10,000 years, the acceptable release limits are 10 times all values in this table.

The sequential nature of these four steps is shown on Figure 2-1. The regulatory criteria for each of these areas and the additional performance objectives for the engineered system specified in 10 CFR Part 60 are briefly discussed below.

2.2 Engineered System Design Requirements

The proposed Rule imposes three major performance objectives on engineered barriers for anticipated processes and events. These are:

- o Contain waste for 1000 years (60.113)
- o Control rate of release after 1000 years (1 part in 100,000 per year, maximum) (60.113)
- o Develop engineered barriers in consonance with retrieval plans (60.133)

The Rule imposes only one major requirement on the actual design process (as opposed to design criteria). This is to require a quality assurance program based upon Appendix B of 10 CFR Part 50 (60.152).

2.3 Design Analysis

The proposed Rule imposes four major design analysis requirements. These are:

- o Analyze the effectiveness of engineered barriers (60.21)
- o Analyze the expected performance of engineered barriers (60.21)
- o Consider expected thermal and thermomechanical response of the host rock and groundwater system in the analysis (60.133)
- o The analysis must provide reasonable assurance that the performance of the engineered barriers will be in conformance with the criteria and objectives (60.101)

2.4 Data and Model Verification

The proposed Rule imposes two requirements on the verification of data and methods in design and analysis. Fulfillment of these requirements must be documented in the SAR. The requirements are:

- o An explanation must be submitted of the measures used to confirm the models used in the analysis (60.21)
- o A justification must be submitted on the selection of the variables and conditions used in design and analysis (60.21)

2.5 Performance Confirmation

The proposed Rule requires that, before and during repository operation, a performance confirmation program be conducted which indicates that the engineered systems are functioning as intended and anticipated (60.140).

The proposed Rule also recognizes that confirmation of the performance of an engineered system which is designed to function over thousands of years "is not to be had in ordinary sense of the word. For such long-term objectives and criterion, what is required is reasonable assurance, making

allowance for the time period, hazards and uncertainties involved, that the outcome will be in conformance with those objectives and criteria."

3 DEFINITION OF ENGINEERED SYSTEM

3.1 Definition of Engineered System Components

Definitions for specific features of the engineered system are provided in 10 CFR 60.2, as follows:

Barrier means any material or structure that prevents or substantially delays movement of water or radionuclides.

Engineered Barrier System means the waste packages and the underground facility. For the BWIP design, this includes the backfill placed around the waste container in the emplacement hole, the backfill and other seals or plugs placed in the storage rooms and access tunnels, and some portion of the host rock immediately surrounding the excavation.

Underground Facility means the underground structure, including openings and backfill materials, but excluding shafts, boreholes and their seals.

Waste Package means the waste form and any container, shielding, packing and other components surrounding the waste form.

There are two boundaries of interest for assessment of release rates from the engineered system: (1) the outer limit of the waste package and (2) the boundary between the underground facility and the geologic setting.

The definition of the waste package may be interpreted to include the tailored backfill placed in the storage hole around the waste canister; thus the waste package boundary would then be the edge of the emplacement hole. The boundary between the underground facility and the geologic setting is currently interpreted as the edge of the mined openings, or a short distance beyond the opening.

The engineered system components may be evaluated at several levels of detail, using alternative models, which are consistent with the environmental scale in which they are intended to function. These environments include:

- o Repository-scale environment.
- o Room-scale environment.
- o Waste package-scale environment.

The repository-scale environment is used to model near-field geologic, hydrologic and geochemical conditions, including the effects of geologic processes and events. Properties of the underground facility and waste packages (hydraulic conductivity, density, thermal load, etc.) may be represented by equivalent values averaged over the area or volume of the facility, based on the waste storage configuration, volume of rock excavated, type of backfill material, etc. This scale of analysis provides input to far-field waste transport assessments and establishes boundary conditions for more detailed analyses.

The room-scale environment is used to model performance within the underground facility, including construction/thermal-induced stress effects, local groundwater flow, geochemical and hydrochemical effects, and the contribution of storage room barrier materials to limiting radionuclide release to the geologic setting. Releases from each storage room are aggregated to determine cumulative releases for repository scale modeling. Boundary conditions for waste package modeling are established.

The waste package-scale environment is used to determine the waste package life and subsequent release of radionuclides from the waste package into the underground facility. This includes a detailed evaluation of metal corrosion rates, water seals (backfill), dissolution or leaching of the waste form under the anticipated range of geochemical/hydrochemical conditions, and all possible waste transport processes (diffusion, advection, colloidal/particulate, etc.) through the waste package materials. The process by which solutes are transported by the bulk motion of flowing groundwater is known as advection. Colloidal or particulate transport refers to solid particles in suspension.

3.2 Engineered System Components

3.2.1 Objectives

The design objectives of the engineered barrier system are (1) to supplement the waste form in meeting the NRC release limits to the geologic setting, and (2) to supplement the waste form and the geologic setting in meeting the EPA limits of release of radionuclides to the accessible environment. The engineered barrier system must meet these two objectives throughout the repository lifetime. The objectives must be fulfilled for the anticipated thermal and radiation environments and within the structural, hydrologic and geochemical environments expected in the repository. In addition, the engineered barrier system must be shown to meet the design objectives for those anticipated processes and events which will influence repository performance.

Because the engineered barrier system must perform in an environment of considerable uncertainty, with potential performance uncertainties of individual components, basic principles must be adhered to in the system design. These include:

- o Engineered barriers should be selected and designed on the basis of established principles (state-of-the-art) in geotechnical, mining, chemical and nuclear engineering.
- o Design of engineered features should not be based on the results of unproven theories or concepts but should be based on testing and proven performance.
- o The design and selection of engineered features should be linked to the major factors affecting performance on the repository scale and major system interaction effects on room and waste package scales.
- o Engineered barrier design and assessment should also take into account features of barrier system performance will be site-specific.

The design objectives and principles require that the engineered barrier design criteria address both deterministic and stoichastic (time-dependent event) considerations. On the deterministic side, the engineered barriers must contribute to system performance even if other features of the geologic repository cannot (such as providing for sorption of specific nuclides not sorbed well by the host rock). Considering the stoichastic events, the engineered barrier system must provide redundant functions in case of failure in the engineered or geologic systems. For example, premature failure of a waste package should not result in an above-limit release through total dependency on a diffusion process or on the sorption properties of a backfill.

3.2.2 Functions of Engineered Barrier Components

The engineered system can perform a number of functions in meeting its design objectives, including:

- o Irreversible sorption of radionuclides by ion exchange.
- o Retardation by equilibrium sorption which allows radionuclide decay time to occur.
- o Dispersion, which reduces peak discharge and spreads releases over time.
- o Permanent bonding within the barrier; for example, by formation of secondary mineral species.
- o Radionuclide holdup by filtering; some backfills behave as semi-permeable membranes.
- o Restrict transport to diffusion by minimizing water flow rates, and limit the diffusivity of the backfill.
- o Provide a low hydraulic conductivity barrier to water (solute) transport.
- o Provide reinforcement to the waste package to withstand crushing forces from rock movement or pore water pressure.
- o Provide repository structural support, relieving stress concentration in the waste package region.
- o Buffer local water chemistry (Eh, pH) to reduce adverse chemical reactions and/or encourage favorable chemical reactions.
- o Retard the escape of corrosion products, to reduce corrosion rates.
- o Retard the influx of oxidants.
- o Provide low resistance heat transfer paths.

For a specific set of site conditions, the role of alternative engineered system components in meeting the overall performance objectives must be defined. The design of each component may then be optimized based on the design objectives that have been determined, incorporating any number of the functions listed above.

4 ASSESSMENT OF RELEASE RATES

Release rates for radionuclides are calculated quantities that are dependent on many complex, interdependent processes and parameters. These include the groundwater flow rates, radionuclide solubility, radionuclide transport processes such as diffusion, advection, colloidal transport, species retardation or irreversible sorption, chemical bonding, radionuclide decay, and many others. Each of these processes and parameters has an uncertainty associated with its value; thus the calculated release rates must also have a potentially large uncertainty. The contribution of both the waste package and the engineered

system to controlling radionuclide release, including data and modeling requirements, are discussed below.

4.1 Release From the Waste Package

The proposed NRC release rate criterion is applied after the required containment time for the waste package (i.e., after 1000 years). The many factors that influence the radionuclide release rate from the waste package can be broadly characterized into three topical areas:

- (1) Waste package life
- (2) Solubility or leachability of the waste form
- (3) Radionuclide transport through remnants of the waste package barrier materials.

4.1.1 Waste Package Life

Package life is important when considering the total mass of short-lived nuclides that will be released to the environment. The range of half-lives of the nuclides in the waste is from approximately 30 years to greater than 1 billion years. Thus, if the package can survive to a time that is many half-lives of a particular nuclide, then that nuclide mass in inventory might have decayed to a sufficiently small quantity to be of no consequence to the total release to the environment.

In order to assess the importance of package life with respect to a particular nuclide, a minimum of five quantities must be evaluated: inventory at emplacement, radionuclide half-life, package failure time, total mass released from the package, and the transport time through the waste package to the underground facility.

The first three quantities listed here determine the inventory at the time of package failure. The total mass released from the package can then be equal to the inventory at the time of failure if the transport processes are fast compared to the nuclide half-life. However, if the transport processes are slow, an additional fraction of the nuclide mass will decay in inventory, thus decreasing the total mass released. For example, for long-lived nuclides such as uranium-238, a package life of one thousand years is not significant because the fraction of uranium decayed will be on the order of 10^{-7} to 10^{-6} during that time. For short-lived nuclides, such as Cs-137, package life is important because the fraction remaining at the end of package life will be less than 10^{-10} of its inventory at emplacement and the mass available for release will be of little significance.

4.1.2 Waste Form Solubility/Leachability

The waste package will be designed to delay the intrusion of groundwater and thus postpone the inception of dissolution or leaching of the radionuclides from the waste form. After the waste package is breached, radionuclide release is limited by the finite leach rate of radionuclides from the waste form. In addition to leaching, the release may be limited by the maximum solubility limit of the radionuclides, particularly for the actinides. In this case the release rate would be lower than the leach rate. Other

factors, such as irreversible precipitation, may further reduce the rate of release from the waste package.

4.1.3 Radionuclide Transport

Failure of all waste packages in the repository will not, in practice, occur at the same time so that the release from the waste packages will be distributed over time. The concept of reliability in determining waste package life is discussed in Appendix P. Furthermore, once a waste package has been breached, the radionuclides must be transported out through the engineered barrier remnants before release to the underground facility or host rock is possible. Engineered barriers may be designed to absorb radionuclides or otherwise affect this process, and the actual release of radionuclides from the waste package will therefore be spread over time. The transport process itself will dilute and allow further decay of the released mass, and a final conclusion must be determined on the consequence of the mass released.

4.2 Release From the Engineered System

Once radionuclides are released from the waste package into the underground facility, the singular function of the engineered barriers is to maximize the residence time of radionuclides within the underground facility and thus allow decay of the nuclides to occur. This has the effect of reducing the rate at which nuclides are released to the geologic setting. It is this release rate that is specified as a performance objective in 10 CFR 60.113.

This delay within the underground facility may be accomplished by using engineered barriers in a number of ways, including irreversible and equilibrium sorption, permanent bonding, filtering, and chemical control. Each nuclide must be specifically examined because of its individual chemical properties. Accomplishing this delay in nuclide travel time requires specific consideration of the hydrological system, and the geometry and hydrological properties of the engineered barrier system. The identified BWIP design of horizontal waste package emplacement for the basalt repository, coupled with a predicted vertical hydrologic flowpath through the host rock means that all delay must be accomplished within the waste package (and its associated engineered backfill). The adequacy of the horizontal emplacement mode, or of any other candidate system, must be closely and defensibly examined to ensure that the entire engineered system performs to the regulatory standards.

4.3. Design Analysis of the Engineered System

The design analysis of the engineered barrier system is based on the quantification of the radionuclide mass transfer from the waste package, through the engineered backfills and other barriers, and into the geologic setting. Quantitative analysis of this mass transfer requires an understanding of each system variable and each transport phenomenon, and results in the predicted behavior of each major system component. Mathematical models have been developed which consider most of the important effects and variables. These models may be conservative in their representation of the release of specific radionuclides to the geologic setting. Care must be taken

in assessing models, to ensure that synergisms within the systems affected by release of radionuclides are also conservatively evaluated.

4.3.1 Release Rate Model Methodology

4.3.1.1 Groundwater Models

The goal of groundwater modeling is to determine boundary conditions for the engineered system and to predict the flow field past the waste package, through the underground facility and, ultimately, through the geologic setting. The rate of flow past the waste package will control the solubility limited release rate after package failure, and the flow velocity through the engineered system will determine the dominating waste transport mechanism.

A good understanding of the site/geological/hydrological conditions is of primary importance, and this must be presented in the form of a conceptual model. Computer codes used to numerically simulate the model must be able to duplicate site conditions (observed from measured data) and changes that will be imposed by repository construction, natural events or human interference.

Additional information on groundwater modeling is provided in Appendices F, H, J, L, M, and O.

4.3.1.2 Mass Transport Models

Calculation of mass transfer from the waste form through the engineered system will require several interlinked computer codes, which, as a minimum, will calculate:

- o Inventory of radionuclides in the waste
- o Degradation and failure of the waste package
- o Leaching of the waste matrix
- o Solubility of radioactive elements in groundwater
- o Transport of waste by groundwater, including the effects of dispersion, adsorption, and chemical retardation.

The mass transfer models must be able to consider all changes in conditions with time. Environmental conditions anticipated for the waste form and metallic waste package components are described in Appendix Q. In order to solve the mass transfer mathematics, appropriate boundary conditions must be specified. The boundary at the waste form is usually described by a nuclide solubility limit or a leach rate (flux) from the waste. Mechanisms of transport of radionuclides from the waste to the backfill are discussed in Appendix R. At the host rock (or geologic setting) the boundary is usually specified by a zero concentration, a flux rate, or a combination of concentration and water flow rate. These boundary conditions, both at the waste or host rock boundary, must be assumed for a specific design, and the use of alternative boundary conditions may yield a different release rate prediction.

The release rate of a radionuclide through an engineered backfill can be driven by a concentration gradient (diffusion, low flow conditions), a

hydraulic gradient (advection, higher flow conditions), or a thermal gradient (Soret effect). Mass transfer will take place at a rate determined by the resistance to mass transfer and the capacitance effects of the medium through which the mass transfer occurs.

There can be three distinct time frames for the occurrence of nuclide release. These are (1) an initial transient release, (2) steady-state release, and (3) inventory depletion when the release from the engineered backfill tails to time equal infinity. The nuclide inventory and thickness of backfill determines if all three time frames can occur. For steady-state release to occur, there must be sufficient mass available from inventory to saturate the backfill. For many nuclides the inventory is not large enough and there will be a transient rise in the release rate followed by a fall to infinity, with no steady-state release. The capacitance of a backfill affects the transient release rate, but has little or no effect on the steady-state release rate for the dimensions of interest and species half-lives.

Analyses of mass transfer through the engineered system, based on transport mechanisms previously discussed, suggest that radionuclides with the highest release rates will be characterized, on a relative scale, by high solubility, by low adsorption potential, by high diffusivity, or by any combination of these extreme parameter values. These three parameters can be controlled or modified to some extent by or within an engineered backfill.

4.3.2 Data Base

The data base to support the necessary and complex design analyses is currently quite limited in several important respects. A stronger data base must be developed which reflects the large number of system variables and, their interdependencies, and which can support the definition of parametric values and uncertainty distributions for use in design analysis.

Quantities of significance which directly affect the release rate from the engineered system include the species diffusivity through the medium, the capacitance (adsorption), and the maximum species concentration in water at the waste. All these quantities are chemical-species dependent which means that the chemical form of the nuclide must be known. The chemical form of the nuclide is determined by the oxidation state, hydrogen ion activity, and composition of the groundwater. Hence, in calculating release rates, a knowledge of the site geochemistry is essential.

Geological and hydrological parameters used to define the hydrological conceptual model, and the boundary conditions for calculation of flow through the underground facility, are also important. In particular, the distribution of hydraulic pressure heads (hydraulic gradients) throughout the geologic setting in which the repository is constructed, and in the host rock, must be known with confidence. Additional information on geological and hydrological data is provided in Appendices F, H, M, and O.

Factors which should be considered when establishing an adequate data base include:

- o Measurement of key parameters demonstrated to affect performance
- o Confirmation that the information obtained from test or analysis measures the required parameter under conditions relevant to those expected in the repository
- o Interdependency of parameters must be recognized and determined
- o Parameter uncertainties must be defined and reduced as much as economically and temporally possible.

4.3.3 Model Verification Requirements

The requirements for repository performance confirmation, including engineered barriers, include data measurement, design testing, and monitoring during the period of operations. No reliance is to be placed on post-closure monitoring. Therefore, assessment of long-term performance of engineered barriers, and demonstration that the NRC performance objectives will be met, will depend largely on predictive models that must be verified using data obtained from short-term tests.

The inaccessibility of the engineered system for long-term monitoring (beyond 80 to 100 years) leads to possibly large residual uncertainties in the data base and boundary conditions used to determine waste package life, waste leaching/dissolution, and transportation of radioactive species to the geologic setting. Many of the physical properties and parameters that appear in release rate prediction models are generally not well known, and variations of values must be considered at early stages of licensing to determine their relative importance on the results of a performance assessment. This can be done by using ranges of values (sensitivity analyses) or parameter probability distributions (uncertainty analyses), based on either analytic solutions to mass transfer or on numerical methods.

The uncertainties in understanding all waste transport phenomena, as well as the variability in the conceptual numerical models, suggests the potential for an additional degree of uncertainty in the engineered system performance assessment. Modeling uncertainties can be reduced by:

- o Simulating problems with known analytical solutions
- o Benchmarking - comparing solutions to complex problems obtained using similar computer codes (e.g., BARRIER/WAPPA, SWIFT/MAGNUM, NUTRAN/CHAI NT)
- o Verifying the conceptual models and computer codes by simulating a monitored event in the real system.

Uncertainties in data and assumptions used in numerical approximations also assures implicit uncertainties in predicted performance of the engineered system. The uncertainties in the waste transport process through the geologic setting are, however, potentially greater than uncertainties associated with waste package lifetime and waste transport through the engineered system. Thus, the models and data which predict engineered system performance must continue to be comprehensively developed. In their absence, it will be difficult, if not impossible, to defensibly predict the engineered system performance.

5 IDENTIFICATION OF AREAS OF CONCERN

The BWIP SCR describes the state of knowledge concerning disposal of HLW in a repository at the Hanford Site and provides a detailed plan for acquiring additional information to resolve site-related issues. The current information base required for evaluating release rates from the engineered system as provided in the SCR is sparse in several important respects. Extensive work will be required, as indicated in Vol. 3 of the SCR, to allow evaluation of the engineered barrier system for the basalt repository. This section of Appendix W identifies several areas of current concern to the NRC with respect to release rates from the engineered barrier system. It focuses on the relative necessity and importance of design and performance attributes of the engineered components of the barrier system. The concerns voiced here are based on the existing information base and/or studies by the NRC and its subcontractors. It is recognized that present concerns over aspects of the BWIP SCR and its treatment of the engineered barrier system may be alleviated as new data and information develop.

5.1 Role of Engineered Barriers in Site Performance

The BWIP SCR emphasizes the important role of natural barriers to minimize release and allow EPA criteria to be met. Chief among the natural barriers is the groundwater travel time to the accessible environment which exceeded 10,000 years in all the studies reported in the SCR. However, it has not been demonstrated with absolute surety that travel times will exceed 10,000 years, and recent work by the NRC, based on BWIP data, suggests that a travel time of 5000 or less years is plausible. Therefore, groundwater travel time may not, by itself, be sufficient to reduce release rates within the first 10,000 years to EPA levels. A careful analysis of the credible range of groundwater travel times at the BWIP site is essential.

Two other important natural barriers emphasized in the SCR are retardation in the host rock and solubility constraints on radioactive concentrations in groundwater. These properties in conjunction with the potentially long groundwater flow times may be shown to limit the release of most nuclides to acceptable levels. However, there are several important radionuclides which may be retarded little in the basalt and which may also have high solubilities (e.g., I-129, C-14 and possibly Se-79 and Tc-99). Evaluation of the role of solubility and retardation (adsorption) is difficult at the present time, since the data base on these phenomena under predicted in situ conditions is extremely limited. Furthermore, the uncertainties in the extrapolation of measured adsorption coefficients and solubilities to calculations of waste transport over 10 km of geologic media must currently be considered large. Uncertainties of several orders of magnitude in applying laboratory estimates of adsorption coefficients to transport calculations have been reported.

Therefore, it is strongly indicated that there is a need for a system of engineered barriers at the Hanford site that can increase confidence in containment of the wastes within the underground facility and provide an important additional margin of safety. The design of the waste emplacement scheme must consider possible variations in groundwater flow rates and direction to ensure that engineered barrier containment objectives can be met.

5.2 Adequacy of Models

Models for assessing release rates from the engineered system are at an early stage of development. Two of the principal very-near-field predictive models, BARRIER and WAPPA, are listed in the SCR as "codes currently under development." A list of features in WAPPA that may require modification for basalt is also provided. Other models, such as those used to predict geochemical conditions, may also require modification to be applicable to the basalt environment. Even when modified, current models may not properly replicate certain physical or chemical processes that are themselves not fully understood.

It is essential that the uncertainties associated with numerical models are clearly understood and their effect on site performance calculations quantified. Numerical uncertainties, associated with the algorithms on which a code is based, can be quantified. The representation of certain physical or chemical processes, such as retardation in basalt and stress-induced rock fracturing, is much more difficult, and it is necessary that the sophistication of present models should be developed hand-in-hand with laboratory and field testing and research. This fact appears to be recognized in the SCR.

5.3 Package Backfill as an Engineered Barrier

Backfill around the waste canisters is identified in the SCR as a potentially important engineered barrier. The backfill is intended to fulfill two functions: enhance canister lifetime and restrict radionuclide releases when canisters are breached. Important properties of package backfill are hydraulic conductivity characteristics, nature of additives, retardation potential and reliability.

Hydraulic Conductivity

The SCR emphasizes the advantages of choosing a low conductivity backfill, which may be able to exclude water from the canister for only about 100 years. Since low groundwater flow conditions at BWIP may well ensure diffusion dominate transport for even a high conductivity backfill, the advantage of the selected low conductivity material should be carefully evaluated in relation to its cost.

Retardation Potential

The SCR emphasizes the importance of waste package backfill as a diffusional barrier to radionuclide release. However, recent work by the NRC suggests that a typical diffusion time for an unadsorbed nuclide through such backfill is about 1 year. Hence, significant retardation is required if the backfill is to appreciably delay release. There are a number of highly sorbed nuclides (Cm, Am, Pu and Th) which may be expected to be contained for long times by the backfill. However, there are also a number of nonsolubility limited nuclides such as Se-79, C-14, I-129, and Ra-226 for which the backfill may be insufficient as an engineered barrier. Reliance on the package backfill as a diffusion barrier for all nuclides is considered to be premature and unsupported.

Additives

The SCR states that additives to adsorb or precipitate some nuclides may have to be added to backfill to ensure compliance with the NRC release criterion, and compliance may not be possible without such additives. However, little support for the feasibility of this approach is provided. There is concern that additives may not prove to be either a feasible or reliable approach and there might be too much optimism on "fixes" to the basic backfill material. The difficulties of reliably tailoring backfill materials to specific functions needs to be emphasized. The SCR recognizes that additional work in this area is required.

Reliability

The waste package emplacement scheme included with the SCR is stated to consider delayed backfilling around the horizontally placed waste packages, and uses a 75:25 mixture of crushed basalt and bentonite pellets. Since the engineered barrier system in the reference design places substantial dependence on the waste package backfill, the reliability of the in-place properties of the backfill will be critical. Delayed backfill placement in the proposed scheme will lead to large uncertainties because:

- o Spalling of rock from the inside of the emplacement hole from thermal stresses may prevent complete backfilling due to blockages
- o Obtaining consistent compaction density, porosity, and hydraulic conductivity values for the backfill around the complete annulus of the hole will be virtually impossible to verify.

No in situ tests of this proposed method have been undertaken to date. In recognition of these potential problems, an alternative emplacement system using pre-cast backfill blocks contained within the waste container is also proposed in the SCR. The relative reliability and uncertainties of these two systems must be carefully evaluated in the repository performance assessment.

5.4 Adequacy of Repository Design

The basic disposal scheme described in the SCR involves horizontal emplacement of canisters in long boreholes stretching between repository tunnels. One advantage of this horizontal emplacement scheme is that it minimizes excavation costs. Offsetting this positive factor, meeting proposed NRC and EPA criteria may be more difficult for horizontal waste emplacement than for alternative schemes such as vertical emplacement beneath storage rooms.

The advantage of the vertical emplacement scheme for the BWIP is that room backfill may be used as an additional engineered barrier. The predicted vertical groundwater flow must pass through the room backfill if it has a sufficiently high hydraulic conductivity relative to the host rock. If the backfill also has a high porosity and good retardation characteristics, it will significantly delay and reduce releases from the engineered system by transporting the waste through a significantly greater thickness of material than it would for package backfills. A further advantage is that the room

backfill will be less affected by the extreme thermal, radiation and geochemical processes occurring in the immediate vicinity of the waste canister.

While horizontal emplacement may prove to be both acceptable and cost-effective; it is considered premature at this stage not to consider room backfill as a primary engineered barrier in a basalt repository.

5.5 Repository Sealing

A key question to be addressed in evaluating requirements for a repository sealing program is whether horizontal transport through the repository is likely to occur. Radionuclide transport through the host basalt flow is likely to be predominantly vertical, enhanced by the thermal effects. If this is demonstrated, reliance on tunnel seals will be minimized (Golder Associates, 1982) and there is strong reason to believe that repository sealing can be accomplished with relatively high permeability backfill materials, rather than expensive, highly "impermeable" seals. A rapid resolution of this question by three-dimensional modeling would permit the requirements for repository seals to be evaluated. The design and performance objectives for repository seals should be developed through a comprehensive analysis program early on in the repository design process.

DEVELOPMENT SEQUENCE FOR ENGINEERED BARRIERS

Figure 2-1

APPENDIX X (RETRIEVAL)

1 INTRODUCTION/OVERVIEW

1.1 Repository in Basalt: Basic Information

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1.2 Retrievability Impacts on Repository Systems

- 1.2.1 Excavation Systems**
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1.4 Summary and Conclusions

1.5 References

APPENDIX X RETRIEVAL

1 INTRODUCTION/OVERVIEW

The goal of a mined geologic waste repository is to ensure that existing and future radioactive waste from civilian activities (including discarded spent fuel from the once-through nuclear fuel cycle) can be isolated from the biosphere and not threaten public health and safety. Isolation of nuclear wastes from the biosphere is to be accomplished through a multibarrier system composed of (a) canistered waste packages, (b) geologic and (c) engineered barriers. Repository performance is based on the combined performance of these individual elements over a long period of time.

In the NRC regulation (Draft 10 CFR 60), a proposal for retrievability of high-level canistered nuclear wastes in geologic repositories is promulgated. The proposal is based on the repository being a new human enterprise in which exists the possibility that mistakes may occur, improved technologies may be developed, better designs may be created, and operational procedures may be improved. With these possibilities, it is desirable to postpone any irreversible (or not easily reversible) decisions until the maximum amount of reasonably obtainable information about how well the repository is functioning and how it can be expected to function to contain and isolate the canistered waste for the periods of time required becomes available. Draft 10 CFR 60.111 addressed this postponement as follows: the geologic repository operations area shall be designed so that the entire inventory of waste could be retrieved throughout the period during which the 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. The staff's purpose is to make sure that if retrieval becomes necessary, that it could be accomplished in compliance with draft 10 CFR 60 and in about the same period of time as that during which they were emplaced.

The retrieval period begins with the initiation of waste emplacement. The function of this period is to allow the retrieval of waste to be a planned contingency operation if data obtained during final construction or waste emplacement phases raises serious questions about the long-term ability of the repository to safely isolate waste.

Much of the information that can be used to verify repository performance will have been obtained before waste emplacement. However, the following three categories of in-situ information are dependent on the waste being emplaced within the repository: (1) waste-induced effects on the geology and hydrology of the site, (2) waste package performance in the host formation, and (3) verification of system operation with waste-filled canisters. The number of years required to verify in-situ geologic and hydrologic response and waste package performance will be site-specific. The verification period depends on physical, chemical, and mechanical considerations such as thermal loading, waste package configuration, and the waste handling processes.

The length of the retrievability period is defined as the maximum period of time that any single waste canister is expected to remain retrievable as part of the planned contingency operation. The period should be as long as is

required to verify confidence in site-specific repository performance after emplacement begins. Thus, the length of the retrievability period depends on site-specific characteristics, repository design characteristics, and the retrieval procedure. Draft 10 CFR 60 proposes that this period be fifty years from the initiation of waste emplacement.

Termination of the retrievability period will not mean that the wastes cannot be removed. Rather, after the required retrievability period, removal will still be possible, but it may gradually become more difficult and costly. However, removal after the retrievability period would not be a planned contingency incorporated into the overall repository operations and would not require periodic demonstration.

1.1 Repository in Basalt Basic Information

The design for a repository in basalt calls for waste to be emplaced horizontally in mined pillars. Backfilling will be delayed to allow the waste canisters to cool and to facilitate the possibility of retrieval.

1.1.1 Definition of Repository Concept

The host geologic medium is basalt. Waste packages shall be placed in about 2 ft. diameter boreholes about 200 ft. long in the pillars between rooms with a number of canisters emplaced per hole. When a storage panel is complete, it will be bulkheaded off and 'trickle' ventilation will be maintained to remove excess humidity and preclude the buildup of dangerous gases. Backfilling would progress sometime between the initial verification period and decommissioning.

1.1.2 Geologic Environment

1.1.2.1 Rock Units

The proposed geologic horizon for repository emplacement at the Hanford Site is the Umtanum (with the Middle Sentinel Bluffs as an alternate location) of the Grande Ronde Basalt. The Umtanum is thought to consist of a single basalt flow, and, as a member of the Grande Ronde Formation, it is among the most areally extensive of the flood basalts comprising the Columbia River Basalt Group. The proposed site lies within the Cold Creek Syncline within the Pasco Basin.

1.1.2.2 Rock Mechanical Properties

Rock strength and thermomechanical properties used for the conceptual design were based on laboratory properties selected from a literature survey. This survey (Agapito et al., 1977) was conducted before initiation of the BWIP laboratory testing program. Laboratory tests have since been done on cores from the Umtanum and Middle Sentinel Bluffs and the strength properties have been reported.

A comparison of the laboratory tests on the Umtanum core as compared to the basalt characteristics used in the conceptual design shows agreement within 15% of all parameters except shear strength parameters.

Full scale and in situ strength tests have not yet been conducted.

1.1.2.3 Hydrogeology

Extensive hydrogeologic investigations and modeling of the Pasco Basin and Hanford Site have been performed and are continuing. The hydrogeologic data presently available for the proposed repository depth of 3,700 ft (1,128 m) are limited. The basalt has very little intrinsic permeability and groundwater flow in the Umtanum will be controlled by the fractures and flow characteristics. Because of the limited subsurface data, the influence of regional structural geology on groundwater regimes has not been fully assessed.

1.1.3 Repository Construction and Layout

As shown in Figure 1, (DOE/SCR 10.4-3), the repository will contain 20 waste storage panels, an experimental panel, and a panel for storage of low level-transuranic waste. A waste panel is an area that will provide space for one year's receipt of nuclear wastes in the form of 520 commercial high level waste canisters and 875 spent fuel canisters. The shape and size of the panel is determined by mining constraints and thermal loading limits. Conceptually, one hundred foot rock pillars will separate adjacent panels and each panel is served by two entries that connect into the two central placement rooms. There will be five shafts for the repository, as follows:

- (1) confinement air exhaust shaft
- (2) confinement air intake shaft
- (3) service shaft
- (4) basalt transport shaft
- (5) waste transport shaft

The selection of a sinking method for these shafts has not yet been reached but is dependent on; final shaft diameters, depth of the shafts, underground geotechnical and hydrological conditions, and technological developments.

Following the completion of the panel, the conceptual design indicates that large diameter holes will be bored horizontally between adjacent chambers in a panel with the waste being emplaced into these boreholes after the panel is completed.

The rate at which canistered wastes are planned to be emplaced is one of the major factors determining the final shaft diameters. This decision must be made early in the conceptual design stage, and will effect many of the repository operations; particularly, emplacement and retrievability.

1.1.4 Canister Arrangement

The waste package that will be used for spent fuel (inside Diameter 12 inches, inside length 13 ft) will contain rods from spent fuel assemblies in a cylindrical canister in a close-packed array. Pins from either 7 PWR (boiling water reactor) or 3 PWR (pressurized water reactors) disassembled fuel assemblies are placed in a canister. These canisters will be placed in the horizontal boreholes.

1.1.5 Thermal Loading

As a result of decaying radionuclides contained in the spent fuel, the waste packages radiate heat. Unreprocessed spent fuel contains fission products which are relatively short-lived and actinides which are generally quite long-lived. As the radionuclides decay to stable isotopes, the number of disintegrations and heat produced will decrease with time. Therefore, the heat produced by a canister will be maximum at the time of emplacement.

The overall thermal load on the repository is determined from the areal extent of the repository, the canister spacing, the age of the waste, and the type of waste (PWR or BWR). To be conservative, it has been assumed that the waste is all 10-year-old BWR. But in reality, waste will be of the two types of varying ages (it is assumed that to avoid uneven thermal loading, individual panels will contain waste of uniform type and age).

1.1.6 Backfilling Timing

Ultimately, the repository will probably be backfilled, with the backfill designed as a barrier (Draft 10 CFR 60.132(i)). Backfill will be placed in the panels and boreholes containing the canistered wastes at sometime after the end of the initial verification period.

1.1.7 Ventilation

In the repository design there are two separate ventilation systems; one for mining development and one for confinement ventilation.

The mining development ventilation system provides air for the shaft pillar area, the main entries and for panel development. The system is a push-pull (multiple fans) with the exhaust air fans located at the surface. Because of high in situ temperatures and the need to provide an environment that mining personnel can work in safely a chilled water cooling system is provided.

The confinement system provides ventilation to support all activities related to the waste handling operations (i.e., transport, emplacement, retrieval). The system is designed to minimize the potential for air leakage between the confinement and development ventilation systems. The confinement ventilation system is also of the push-pull variety.

The exhaust air from the confinement system is drawn up the exhaust shaft by the confinement exhaust fan and is vented out to the atmosphere. If radiation is detected in the exhaust air, then the air would be sent through high efficiency particulate air filters.

After a room has been filled to capacity with waste, it is sealed off and only trickle ventilation to that room is maintained.

The confinement system would provide ventilation for all underground activities associated with mass retrieval of waste.

1.1.8 Retrieval Systems

Draft Title 10, Part 60 of the Code of Federal Regulations (10 CFR 60) requires that repository operations be designed so that the entire inventory of waste could be retrieved on a reasonable schedule, starting at any time up to 50 years after waste operations are initiated. This statement defines full retrieval. However, it may also become necessary sometime to retrieve on a limited basis (e.g., a few canisters, a single room, or a single panel); for the purpose of this appendix, this scenario is designated as local retrieval.

1.2 Retrievability Impacts on Repository Systems

1.2.1 Excavation Systems

If storage rooms are bulkheaded after being filled with waste canisters, a means of access will be maintained to monitor the storage atmosphere. Bulkhead design must meet certain criteria to prevent deterioration from extreme differential temperatures on either side. It is most likely that the bulkhead will be made of concrete and contain reinforcing steel, keyed into the side walls. Upon retrieval, or at decommissioning, the bulkhead will be removed and the panel backfilled. The removal of such a wall can be done in several ways although blasting may be the least desirable, possibly causing damage to the entry. Drilling holes for rock breaking devices may be the safest removal method, and does not require elaborate equipment or highly skilled labor. Bulkhead removal may be tedious but it is well within present technology. Certain precautions must be taken to protect personnel from sudden exposure to the higher temperature behind the bulkhead. Precooling of the panel is necessary before equipment can enter the area.

1.2.2 Equipment Systems

Retrievability impacts on equipment systems can best be identified with the aid of a flow chart shown in Figure 2. Each basic repository operation is given an identification number to facilitate an event's impact on all systems. When mining development is complete, the only active operations are those involved with storing canisters.

The different levels of retrievability (local or full) vary greatly in their impact on repository operations. If local retrieval of canisters is necessary for any reason, then it must take place concurrently with storage operations. Unless new equipment is obtained for the task, the machines used for emplacement will be utilized for retrieval thus slowing the normal storage rate. Retrieval of breached canisters will require "hot cell" or shielded equipment and decontamination equipment for the storage area. Transporting these canisters to the surface will require use of the crane hoist and surface handling facilities. These systems will be unable to perform their normal operations for handling canisters and a delay of repository storage activities will occur.

Full retrieval of canisters can be planned systematically for a full storage room or for the full repository, starting with the oldest storage rooms. Because the same handling equipment will be used for the full retrieval operations as for emplacement, an operating schedule can be defined, as no

interference from other operations should exist. If however, many canisters are breached, retrieval will be more complex due to contamination, but the special equipment required for this task will be used for the life of the retrieval operations. Generally, a repository committed to one operation at a time (e.g., all mining completed canister storage only, retrieval only etc.) makes for much more efficient operations than if local retrieval is concurrent with mining.

It is unclear at this time how a canister in a 200 ft horizontal hole can be retrieved. Perhaps a telescopic arm can reach to the extreme distance, but if the canister is frozen in place due to excessive rock stress, retrieval may be impossible. Horizontal storage in holes approaching 200 ft makes the option of overcoring a breached canister very difficult. If overcoring is to be used for retrieval, it must be taken into account that the drift for horizontal storage is about 30 feet wide which necessitates breaking the overcore numerous times before attaining the desired length. Breaking the rock mass will require a special operation, as well as additional work to handle the broken core.

1.2.3 Facilities

If mining development and waste emplacement are concurrent operations, then the reason for full retrieval will most likely preclude additional mining. The modular concept of repository operations keeps the two systems entirely separated to the extent that equipment for each system uses different haulageways and hoisting shafts. Facilities such as haulage ways, loading lines, skips, and other equipment for handling mined rock will not be affected by local retrieval, and may be temporarily or totally stopped during full retrieval.

The area most likely affected by local retrieval would be the shaft area where full transfer casks would be handled, hoisted and lowered, and the mined rock hoisted. Retrieved canisters may be breached, thus compounding the impending congestion.

1.2.4 Ventilation Requirements

In the repository, ventilation is provided only in the central access of a panel after storage has been completed in the panel. The individual panels are bulkheaded but not backfilled. The impact of retrievability on the ventilation system for this design depends on several factors:

1. whether development operations have been completed
2. whether retrieval is local or full
3. whether placement operations have been completed

If development operations have been completed, then there may be no reason to retain two ventilation circuits and hence the air volume capacity of the entire mine air circuit is available, if needed, for waste placement or retrieval operations. Conversely, if development operations are in progress, only the capacity of the waste air circuit is available for placement and local retrieval operations.

If full retrieval is initiated, then by definition both development and placement operations cease and so the total ventilation capacity of both mine and

waste circuits can be used for retrieval operations. Similarly, if placement operations have been completed prior to initiation of retrieval, then the combined capacity of the mine and waste air circuits can be used for retrieval if necessary.

After room bulkheads are breached, pre-cooling will be required before retrieval takes place. The refrigeration and air volume capacities required for pre-cooling depend on the temperature of the rock, the temperature of the intake air, the acceptable temperature for the exhaust air, and the desired rate of cooling.

If local retrieval is required while both storage and development activities are in progress, the total mine air circuit is not available, and hence it is necessary to verify that there is sufficient capacity in the waste air circuit. The worst case could occur in the final year of development operations. This would mean that all panels were bulkheaded except for the central access panel, one panel for storage operations, and one panel for retrieval operations. The ventilation system must have the capacity to meet the requirements of this worst case.

1.2.5 Backfill

Backfill will be placed in the rooms sometime between completion of the initial verification period and decommissioning.

Full retrieval would impact backfilling, in that if all the waste is removed, it is no longer necessary to isolate the repository and hence backfilling is no longer required.

In the case of local retrieval, backfill would still be required even though a room or panel had been emptied of waste. This is to ensure that the room or panel does not become a preferential pathway for the migration of radionuclides.

1.2.6 Equipment Requirements for High Temperature and Radioactive Environment

High temperatures from canisters in storage rooms will not be encountered during retrieval as long as rooms are pre-cooled and are well ventilated. For a full retrieval operation, the same equipment can be used as for emplacement without modification for high temperature.

Radioactive environments will require special shielding of equipment for operator safety. Decontamination facilities will also be necessary for service equipment, storage areas, mine water, and exhaust air.

1.2.7 Ground Support

Theoretical analyses and empirical evidence from other mining of tunnels suggest that there may be a need for rock support. However, there is no experience in the construction and support of tunnels in basalt at the proposed repository depth. The conceptual design proposed the use of a rock support scheme which includes rock bolts and shotcrete.

It is not known how the elevated rock temperatures will affect the stability of either the bolts or the shotcrete. Assuming resin bolts are used, stability of such bolts for periods of 50 years even at the temperatures commonly encountered in mines cannot be guaranteed since they have only been in use for about 25 years.

Experience does exist with cement at elevated temperatures and standards exist for its use in nuclear reactor vessels (ACI 359-77). Therefore, it may be warranted to use cement-grouted bolts and shotcrete containing cements which satisfy ACI 359-77. Use of cement in the bolts would also limit difficulties which might occur due to differential thermal expansion between the steel, the bonding agent in the bolts and the rock (concrete has a coefficient of thermal expansion intermediate between those of steel and basalt whereas resin has a much greater coefficient of thermal expansion than steel or basalt). However, cement grouted bolts do not provide as good a bond between the steel and the rock.

In any case, it can be expected that over a 50-year period some deterioration of the rock reinforcement will occur and minor roof falls may result. Where such has occurred, it will be necessary to remove the debris and provide renewed support prior to commencement of retrieval operations.

Seepage of groundwater towards the mined openings may occur. With time this could result in a buildup of pore water pressure on the shotcrete liner, which could result in deterioration of the shotcrete by chemical action. This could be minimized by curtain grouting at the time of construction of the rooms.

1.3 Adequacy of Incorporated Retrieval Systems or Allowances

1.3.1 Local Retrieval

Radionuclide leakage can occur from defective canisters during storage and necessitate retrieval. A manufacturing error, for example, could cause premature breakdown of some canisters in a storage room. Bulkheaded but unback-filled rooms would permit the use of the same equipment for emplacement and retrieval procedures, provided rooms are cooled prior to retrieval. It is most likely that the canister transporter and "hot cell" equipment will be necessary for breached canisters. Unless the leaking canister is the one closest in the hole to the storage room, retrieval of a leaking canister may require retrieval of many of the canisters emplaced in the hole.

As was discussed in Section 1.2.2 retrieval of breached canisters by overcoring the holes is very difficult with horizontal holes containing more than one canister. A possible method would be to have a piece of equipment pushing from the backreaming rooms as well as having the transporter and transfer cask in the storage room.

1.3.2 Full Retrieval

Full retrieval of waste canisters will need planning and preparation but it will not necessarily be difficult because all repository resources can be committed to the operation. The possibility exists that future technology could create a use for the waste or underground storage may prove unsatisfac-

tory thereby causing the need for decommissioning. Full retrieval should not require special equipment unless events such as excessive rock movement crushes canisters; inundation of the repository due to intersection with a previously undetected water-bearing fault; or the breach of the canisters from corrosion occurs.

1.3.3 Bases for Retrieval

The technical considerations that must be addressed in establishing a retrievability period are derived from an understanding of conditions which could lead to a decision to retrieve emplaced waste. As a basis for evaluating the retrievability issue, a number of scenarios can be postulated. The occurrence of any one of these is unlikely, since extreme care must be taken throughout the siting and design verification processes to minimize the likelihood of such events.

The conditions which could lead to a decision to retrieve emplaced waste may be categorized as follows: (see Table 1)

- o Natural Events and Processes. The occurrence of totally new, unknown, and unexpected natural phenomena in the environment of an operating repository could render it unusable.
- o Geologic and Hydrologic Response to Excavation and Waste Emplacement. The design of the repository will be based on data obtained from sampling and testing and on accepted thermal, mechanical, and hydrologic models. Designs will incorporate margins of safety to accommodate reasonable assumptions of inaccuracies in such design bases. Nevertheless, abandonment of the repository, or a portion of the repository, could conceivably be dictated if performance characteristics indicate that the required degree of confidence in the predicted performance could, for some reason, no longer be provided.
- o Predicted Waste Package Performance. Post emplacement evaluations could indicate that certain waste packages have defects or that the engineered barrier design is not performing as predicted. Retrieval of some defective waste packages or of all emplaced waste would be dictated in this event.
- o Repository System Operation. The final integrated system of the first repository could conceivably be judged not operable due to either an uncorrectable inadequacy of the design basis or small but chronic inadequacies that, with time, build to an intolerable level.
- o Malicious or inadvertent human intrusion and repository disruption. Human-caused events such as construction, sabotage could conceivably affect the integrity of the repository.

1.4 Summary and Conclusions

Draft Regulation 10 CFR 60 requires that geologic repositories be designed to preserve the option of retrieving all of the emplaced waste, starting at any

time up to fifty years after waste emplacement is initiated until decommissioning. The design must also permit the entire inventory of waste to be removed in about the same period of time as that during which the wastes were emplaced.

Retrieval appears to be feasible. Alternative retrieval technical approaches vary widely and there is considerable uncertainty about the feasibility of some of them. To avoid delays in the licensing process, it is essential to identify very early in DOE's conceptual design process, those features which should be incorporated into the repository to allow for waste retrieval.

APPENDIX Y (IN SITU TESTING)

1 INTRODUCTION

2 APPROACH

3 DETERMINATION OF INFORMATION NEEDS

3.1 Critical Repository Design and Construction Engineering Variables

3.2 Key Issues Which Impact the Design of the In Situ Testing Program

3.3 Significant Characteristics Which Impact the Resolution of Key Issues

4 AVAILABLE TEST METHODS

5 CONCLUDING REMARKS

TABLES

FIGURES

GLOSSARY

1 INTRODUCTION

The purpose of Appendix Y is to outline the NRC perspective on the role of in situ testing in basalt at Hanford, Washington. These tests will be conducted within an underground test facility at the prospective repository horizon and an exploratory shaft from the surface to this horizon. Plans for the in situ test program in basalt have been presented by the U.S. Department of Energy (DOE) in a Site Characterization Report (SCR) in November 1982.

This Appendix describes the approach and methodology developed by the NRC for the selection of tests. The types of tests which might be considered, and the details of performing and interpreting these tests, forming part of a reasonable in situ test program for License Application (LA) are presented. The methodology and rationale for the design of a reasonable in situ test program to be conducted between SCR and LA is largely based on a more detailed report by Golder Associates. That report, "In Situ Test Programs Related to Design and Construction of High Level Nuclear Waste (HLW) Deep Geologic Repositories" (NUREG/CR-3065), includes a tentative set of subsurface tests for a basalt site at Hanford. Based on a preliminary evaluation of these information needs for LA at Hanford, Washington, an in situ test facility to accommodate a suitable testing program has been suggested ("Relationship of an In Situ Test Facility to a Deep Geologic Repository for High Level Nuclear Waste," Report by Golder Associates to the NRC, NUREG/CR-2959, October 1982).

Any deep geologic repository for the permanent disposal of high level nuclear waste must be designed to achieve certain performance objectives. These relate to both the short term construction and operation of the repository and to its long term waste containment and isolation functions. The in situ test program should address the particular technical issues which need to be resolved specifically for LA and should provide information to reduce the level of uncertainty on technical questions and repository system performance to an acceptable level.

There are two primary methods of reducing the uncertainty in repository performance:

- o by selecting a suitable site
- o by appropriately designing, constructing, and operating the repository.

The response of the repository is a result of an interaction of both engineered components and site characteristics. Thus, optimization of the performance of the repository and the assessment of the attendant information needs, to be met by the in situ testing program, must consider the site and the repository structure as an integrated system.

The general objectives of the in situ test facility are to:

- o provide access to the repository horizon
- o provide information on constructibility and performance of shafts, tunnels, and underground openings
- o allow complete characterization of the repository horizon, as well as overburden

- o provide technical data and validate the overall repository design assumptions and predictive models for both short- and long-term performance.

In this context, the in situ test program should emphasize the importance of directly evaluating the proposed repository horizon using both representative volume testing of the rock mass and representational characterization of the encompassing site.

2 APPROACH

The approach to the selection and design and selection of tests forming part of an in situ test program conducted during site characterization is based on a defensible rationale. This rationale consists of:

- o establishing the information needs for License Application at Hanford
- o assessing the capabilities of available tests to meet the specific information needs
- o matching the capabilities of specific tests to the perceived information needs.

The information needs result from the uncertainties in the prediction of repository system performance. To establish the information needs, it is first necessary to assess the currently available information and determine the associated uncertainty in predicting each aspect of the repository system performance. The additional information judged necessary to improve the predictability of performance will be a function of the significance of any information component to repository performance and the capability for reducing the level of uncertainty in that particular information component.

With reference to the composition of the information needs and the consequent testing requirements, there is no unique set. The choice of available tests to adequately reduce the level of uncertainty in performance prediction will depend on:

- o the sensitivity of repository performance to any particular information component
- o the cost-effectiveness of obtaining information of suitable accuracy and reliability
- o the accuracy of the test method
- o the possibility for reducing the uncertainty in any one information component.

Information needs may thus change with time according to how the existing information is being updated and supplemented by current work programs, or improvements in the capabilities of tests which fulfill related information needs.

Tests may satisfy information needs by:

- o simulating various aspects of the repository construction/operation
- o assessing the site characteristics (e.g., hydraulic conductivity) for use in numerical modeling of repository performance

- o providing direct verification of predictive numerical models.

The testing approach further requires that the capabilities of the available tests, with respect to responding to the information needs, must be assessed. It is essential that the test data be reproducible and that procedures be established to resolve conflicting test results. From a comprehensive list of available tests and associated capabilities, appropriate in situ tests can be identified which adequately respond to the perceived information needs for License Application at Hanford. The selected tests must then be integrated into a reasonable in situ test program.

Both information needs and test capabilities will change with time as a result of:

- o the supplementing and update of available information by current work
- o improvement in the capabilities of tests
- o improvements in the quality of other performance-related information components.

Therefore, the in situ testing program will evolve with time and should be flexible enough to accommodate such changes efficiently.

3 DETERMINATION OF INFORMATION NEEDS

The establishment of the information needs involves a number of logical steps:

- o identification of critical engineering variables which, in conjunction with site characteristics, will determine repository system performance.
- o determination of key issues which need to be resolved in order to demonstrate achievement of the short- and long-term repository system performance objectives
- o identification of the characteristics of a site which will have a significant impact on the evaluation of the key issues. This also involves an assessment of the relative importance of the characteristics.

The relationship of these steps is given in Figure Y.1.

3.1 Critical Engineering Variables for Repository Design and Construction

The primary engineered components of the repository which must be designed and constructed so as to optimize performance are:

- o surface facilities
- o underground facilities (including engineered barriers)
 - shafts
 - tunnels/caverns
 - waste packages.

Only underground facilities are addressed in the assessment of in situ testing requirements. Those engineering variables which are perceived at the conceptual design stage to have a significant and cost-effective impact on repository performance are judged "critical." These are listed in Table Y.1. These variables should be focused on and emphasized in the development of the in situ testing program.

3.2 Key Issues which Impact the Design of the In situ Test Program

Key issues are those which must be adequately resolved to meet the repository performance objectives. The key issues which impact the design of the in situ test program include:

- o Constructibility. Can an adequate facility be constructed in a timely and safe manner?
- o Thermal Response. Can the temperature field be adequately predicted as a function of time to use as input to the mechanical, hydrologic, and geochemical models?
- o Mechanical Response. Can the stability and deformation of underground openings be adequately predicted for both the construction/operation and isolation/containment periods?
- o Hydrologic Response. Can an adequate prediction be made of the resaturation time of the repository and of the long-term groundwater flow through the repository?
- o Geochemical Response. Can the nature and extent of the geochemical response of the engineered barriers and rock be adequately predicted?

These key issues can be resolved by identifying the relevant repository engineering variables and site characteristics and then establishing the testing requirements which address them.

3.3 Significant Characteristics which Impact the Resolution of Key Issues

The evaluation of which characteristics are considered significant to meeting the performance objectives takes into account the following attributes:

- o availability of design/construction techniques which allow for a conservative assumption of the value of the characteristics
- o the sensitivity of the performance prediction model to the value of the characteristic
- o uncertainty in the representation of the phenomenological laws of nature by the performance prediction model
- o cost-effectiveness of measures to reduce the uncertainty in the assessment of the characteristic.

Two types of characteristics are identified. Those which describe the:

- o geologic setting of the site
- o the response/behavior of the site.

For example, the geologic setting includes the in situ hydraulic head, stress and temperature fields, lithology and discontinuity structure of the rock, and the pore fluid characteristics. The response characteristics are those which describe the phenomenological behavior of the rock and engineered systems, e.g., mechanical, thermal, hydrologic, and geochemical.

The assessment of the response characteristics should consider a number of features of these characteristics which for the rock mass and the engineered barriers may have a major impact on the design of the in situ testing program, namely:

- o anisotropy
- o dependence of characteristic values on time, stress level, pore pressure, temperature, and radiation dose
- o scale of measurement of characteristic
- o variability of properties on the scale of the repository.

The inhomogeneity and discontinuous nature of rock masses is such that the last two features are extremely important in properly measuring and utilizing the values of characteristics. These two features, discussed further in Section 4, are expected to dominate the scope of the in situ testing required to meet the perceived information needs.

The emphasis in the design of the in situ testing program with regard to both the selection of tests and their conduct will depend on the relevance of these characteristics to the key issues previously identified, i.e., on the sensitivity of the outcome of the key issues to the values of the characteristics. Such estimates of sensitivity are necessarily only preliminary at this stage. However, the explicit recognition of the interrelationship between key issues and characteristics, as given in Table Y.2, for example, is an initial step in the formulation of the information and testing needs. This preliminary assessment of the significant characteristics recognizes the following distinctive features of the basalt site at Hanford, Washington:

- o relatively complex geology (flow structures)
- o potential for tectonic activity
- o high horizontal in situ stresses
- o high in situ temperatures
- o proximity to a major water source
- o highly fractured rock mass, especially vertical cooling joints. Despite the strong and impermeable nature of the intact rock, these fractures dominate the mechanical, hydrologic, and geochemical response.

Not all characteristics which are significant to repository performance may impact the selection of the in situ test program. For example, tests may not be available for reducing the uncertainty in the assessment of a significant characteristic in a cost-effective manner. This may be because a suitable test is not available, the uncertainty is already low, or the accuracy of the predictive model which uses the characteristic as input is poor. Characteristics with major significance and which can be most effectively addressed by an in situ test should be given the highest priority in the formulation of the program.

4 AVAILABLE TEST METHODS

There are typically a variety of test methods available for assessing the identified significant characteristics. These methods can be categorized as:

- o surface tests
- o borehole tests
- o laboratory tests
- o subsurface tests (from an adit or shaft).

Differences between the various tests related to the uncertainty in the assessment of values of characteristics is primarily a result of the following factors:

- o Surface Tests
 - representative volumes are readily interpreted
 - minimal sampling disturbance
 - data must be extrapolated to great depths
 - poor resolution
 - cannot test characteristic for a range of environmental conditions.
- o Borehole Tests
 - able to effect large scale (regional) characterization
 - test volume often unrepresentatively small
 - limited ability to vary environmental test conditions
 - poor control of test due to remoteness
 - drilling disturbance may be significant.
- o Laboratory Tests
 - test volume often unrepresentatively small
 - undisturbed samples difficult to obtain
 - able to test for a wide range of conditions.
- o Subsurface Tests
 - able to test representative volumes
 - accurate evaluation of local rock mass properties
 - minimal sample disturbance.

A comprehensive list of available tests which can be used to evaluate the values of characteristics is given in Table Y.3. The limitations of these tests should be recognized when analyzing the test results to obtain a design input value.

Each of these test types has limitations in the assessment of characteristics. These limitations may be partially overcome in certain instances by using a special category of in situ tests which effectively represent a full scale simulation of expected repository construction or operation conditions (see Figure Y.1).

Two special features of rock masses, their inhomogeneous and discontinuous nature, have a very important bearing on the types of tests which are best able to establish characteristic values with low uncertainty over the region of repository influence.

Inhomogeneity requires that, as well as determining the characteristic value, testing must establish the variability of this value and the spatial distribution within the important zone of influence. This representation of site conditions requires that some form of index testing be calibrated with more precise and reliable tests, and then conducted on an extensive scale.

The discontinuities present in a rock mass strongly influence its behavior. To properly characterize the response properties of the rock mass, it is necessary to include within the sample a sufficient number of discontinuities

so that individual features do not discretely influence the test outcome (e.g., hydraulic flow, failure mechanism, etc.). The sample size which allows the rock mass to respond in a pervasively uniform, although not necessarily isotropic, or quasi-continuum manner is termed the representative elemental volume (REV). The size of the REV will depend on the rock type, the discontinuities present, and the characteristic being measured.

If possible, in situ tests on the rock mass should be at REV scale or bigger. Where this is not possible, a number of different sample sizes should be tested to establish the scale effect. This data can then be extrapolated to determine the characteristic value at the REV scale.

An alternative approach to assessing the large scale properties of the rock mass involves separate measurement of the properties of the two components, i.e., the intact rock and the discontinuities themselves. These are then combined in an analytical or numerical model of the composite system to determine the global response characteristic.

The adoption of both approaches is common and helps to reduce the uncertainty of characteristic assessment. However, the more direct approach of testing the rock mass at the REV scale is much more reliable and generally preferred.

5 CONCLUDING REMARKS

A defensible rationale has been developed and demonstrated for the selection of available tests to be considered in an in situ testing program for a repository in basalt at Hanford, Washington. This rationale involves identifying key issues defining repository performance, establishing the information needs to adequately resolve these key issues, and developing an in situ testing program that is best able to meet these information needs given the time and cost constraints.

The importance of having a defensible rationale for selecting and designing the in situ test program is emphasized. Other approaches are possible and the assessments made herein may not be universally shared. However, the rationale should be clearly outlined so that specific areas of technical disagreement can be readily identified and resolved.

The actual selection of tests that will be included in an in situ test program will be a function of the information needs and test capabilities at that time. Both needs and capabilities can be expected to change during planning and conduct of the program. Hence, a flexible program, able to take into account technological improvements, design changes, and new information on site conditions will have a considerable beneficial impact on the cost and quality of information obtained prior to LA.

Glossary

Characteristic:	Aspect of ground or environment quantitatively or qualitatively describing repository site.
Critical Engineering Variable:	Engineering variable which has a significant impact on the level of confidence in satisfactory repository performance.
Engineering Variable:	Engineering aspect of repository design or construction which can be altered by the engineer (e.g., size, shape, and orientation of underground openings).
Information Needs:	Additional information needed to sufficiently reduce the uncertainty in predicted repository system performance.
In Situ Test Program:	Consists of a suite of appropriate in situ tests conducted within an in situ test facility (after initial SCR submittal and prior to License Application) to adequately response to the information needs and thus resolve key issues.
Key Issue:	Question, related either to short-term construction/operation or long-term waste containment/isolation performance, which influences the design of critical engineering variables.
Repository System:	Consists of all components which contribute to performance, i.e., the site characteristics and engineered components.
Representative Elemental Volume (REV):	Volume of rock mass which is sufficiently uniform in material and discontinuity features such that when tested responds in a quasi-continuum manner.
Response Characteristic:	Parameter which describes the response or behavior (i.e., mechanical, thermal, hydrologic, and/or geochemical) of a volume of material. These characteristics are strongly related to the physical characteristics of the material.
Significant Characteristic:	Characteristic or response characteristic which has a significant impact on the resolution of key issues, and thus influence design of critical engineering variables. These characteristics, in conjunction with the engineered components, will determine repository system performance.

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**RATIONALE FOR DEVELOPMENT OF
IN SITU TESTING PROGRAM**

Figure Y.1

**CRITICAL REPOSITORY DESIGN AND CONSTRUCTION
ENGINEERING VARIABLES**

Table Y.1

**CHARACTERISTICS WHICH IMPACT
THE RESOLUTION OF KEY ISSUES**

Table Y.2

**TEST METHODS AVAILABLE FOR ASSESSING
SIGNIFICANT CHARACTERISTICS**

**Table Y.3
1 of 4**

**TEST METHODS AVAILABLE FOR ASSESSING
SIGNIFICANT CHARACTERISTICS**

**Table Y.3
2 of 4**

**TEST METHODS AVAILABLE FOR ASSESSING
SIGNIFICANT CHARACTERISTICS**

**Table Y.3
3 of 4**

**TEST METHODS AVAILABLE FOR ASSESSING
SIGNIFICANT CHARACTERISTICS**

**Table Y.3
4 of 4**