B0287

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Distribution:
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Original not rec'd

Dr. D. J. Brooks
Geotechnical Branch
Office of Nuclear Material
Safety and Safeguards
U.S. Nuclear Regulatory Commission
Room 623-SS
Washington, D.C. 20555

Dear Dave:

Enclosed is the July 1987 progress report for B0287, Technical Assistance in Geochemistry.

Sincerely,

A. D. Kelmers/jp

A. D. Kelmers, Project Manager
B0287 Technical Assistance in Geochemistry
Chemical Technology Division
Bldg. 4500N, MS-268; FTS 624-6870

ADK:jts

cc/encl: Office of the Director, NMSS (Attn: Program Support Branch)
Division Director, Division of High-Level Waste Management, NMSS, NRC (2) ✓
R. L. Ballard, Chief, Technical Review Branch, NMSS, NRC
J. W. Bradbury, Technical Review Branch, NMSS, NRC
G. F. Birchard, Waste Management Branch, RES, NRC
A. P. Malinauskas, Director, NRC Programs, ORNL

4016

08/06/87

PROGRESS REPORT FOR JULY 1987

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT STAFF: J. G. Blencoe, R. M. Gove, G. K. Jacobs, R. E. Meyer, V. S. Tripathi, and K. L. Von Damm

PROJECT MANAGER: A. D. Kelmers
Chemical Development Section
Chemical Technology Division
OAK RIDGE NATIONAL LABORATORY, Operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)/NRC #50 19 03 01

OBJECTIVE:

The objective of this project is to provide technical assistance to the NRC in the evaluation of geochemical information pertinent to the candidate high-level-waste geologic repository sites. The project emphasizes the collection and review of key information to provide input to the NRC analysis of technical issues regarding the geochemical aspects of high-level-waste geologic isolation, and review of site selection and repository licensing documentation.

TECHNICAL HIGHLIGHTS:

Geochemistry Issues:

Draft Letter Reports analyzing the geochemistry issues for the Yucca Mountain site and the Hanford Site are being prepared. Six issues have been defined that cover all regulatory aspects of site characterization and selection, and of repository construction, operation, and closure. The six issues are:

(1) What are the ambient geochemical conditions and processes in the geologic setting?

(2) What are the geochemical conditions of the engineering materials (packing, backfill, and seals) that may be utilized in repository construction, operation, and closure?

(3) What are the changes in the geochemical conditions and processes in the disturbed zone that may occur over time as the result of repository construction, operation, and closure, and how

may these changes affect the anticipated repository performance?

(4) How will the changes in the geochemical conditions and processes that may occur over time as a result of repository construction, operation, and closure affect the anticipated performance of the engineering materials (packing, backfill, and seals) utilized in the repository?

(5) What are the geochemical conditions and processes that may affect the radionuclide source term at the boundaries of (1) the waste packages during the containment period and (2) from the engineered barrier system in the post containment period, and how may the anticipated repository performance be influenced?

(6) What geochemical conditions and processes affect the transport of mobilized radionuclides through the geologic setting and the release of radionuclides to the accessible environment after disposal, and how may the anticipated repository performance be influenced?

Major report sections for the six issues at each site are:

(1) Regulatory Rationale,

(2) Data and Information Needed to Analyze the Issue,

(3) Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information, and

(4) Precision and Accuracy of the Methods, Strategies, and Approaches

With this monthly report we transmit (Enclosures 1 and 2) the draft Letter Reports for both sites containing the added sections n.n.3, Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information. Draft Letter Reports for both sites containing sections n.n.1 and n.n.2 have been previously transmitted. We are now working on sections n.n.4, and have retitled these to read: Precision and Accuracy of the Methods, Strategies, and Approaches.

Hydrazine Data Review at BWIP:

The data review was held at BWIP on July 21-22. A draft Meeting Report describing the meeting, summarizing the information reviewed, and containing recommendations for possible means of resolving open concerns is transmitted with this progress report (Enclosure 3). This report will be finalized after receipt of comments from the NRC.

Transport Modeling:

One- and two-dimensional grids have been created for the assessment of coupled geochemical-transport models. The 1-D grid will be used for sensitivity analyses to help assign values to the geochemical parameters that will be used in the more time-consuming and costly 2-D runs. The chemical systems/parameters to be modeled include Pu, Np, U, CO_3^{2-}, Ca, pH, and Eh. Goethite is being used as a analog for adsorbent minerals typically found in rocks. The effect of redox changes on radionuclide mobility and retardation will be illustrated. The simulations will illustrate how comprehensive geochemical reactions can be coupled to transport models on realistic scales, and that the comprehensive approach to transport modeling yields a better representation of geologic systems and thus, more defensible results than the more commonly used Kd approach. The Kd approach may significantly underestimate potential concentrations of radionuclides in solution. This weakness of the Kd approach may be especially important now that the EPA standards have been determined to be inconsistent with previously established drinking water standards.

General:

The topical review on the solubility of radionuclides (NUREG/CR-4024) was transmitted in final form on mats with the May progress report. The topical review on matrix diffusion, being prepared in conjunction with Jerry Grisak of Intera Technologies Inc., is being revised and expanded to include a discussion of the relationship between performance measurement and matrix diffusion parameters. We are awaiting revised text from Dr. Grisak. The topical review on the geochemical conditions at the Hanford Site will be revised when the NRC review of the draft manuscript is received.

MEETINGS AND TRIPS:

A. D. Kelmers attended the data review at Richland, WA, on July 21-22 to review information on the experimental use of hydrazine to establish reducing redox conditions in radionuclide sorption tests.

REPORTS AND PUBLICATIONS:

None

PROBLEM AREAS:

None

COST/BUDGET REPORT:

Expenditures for July were not available at this time. A detailed cost/budget report will be forwarded under separate cover.

08/06/87

PROGRESS REPORT FOR JULY 1987

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MEETINGS AND TRIPS:

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REPORTS AND PUBLICATIONS:

None

PROBLEM AREAS:

None

COST/BUDGET REPORT:

Expenditures for July were not available at this time. A detailed cost/budget report will be forwarded under separate cover.

LR-287-nn
nn/nn/87

LETTER REPORT

TITLE: Geochemistry Issues for the Yucca Mountain Candidate High-Level Waste Repository Site

AUTHORS: G. K. Jacobs, A. D. Kelmers, and K. L. Von Damm

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: A. D. Kelmers
Chemical Development Section
Chemical Technology Division
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MARTIN MARIETTA ENERGY SYSTEMS, INC.

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)/NRC #50 19 03 01

SUMMARY

This letter report describes geochemical technical issues (Section 3, Geochemistry Issues, in the Nuclear Regulatory Commission (NRC) hierarchy of geotechnical issues) for the Yucca Mountain candidate high-level waste repository site being characterized by the Department of Energy (DOE). These issues are derived from DOE guidelines, NRC rules, and Environmental Protection Agency (EPA) standards that explicitly or implicitly indicate a need for geochemical information relevant to (1) site characterization and selection, and (2) construction, operation, and closure of a repository. The issues are focused on geochemical conditions and processes that have a direct bearing on repository containment requirements and performance

objectives, and the issues are related to repository performance at various stages in time. The ambient geochemical conditions and processes, and the changes in these geochemical conditions and processes which may occur over time as a result of construction, operations, and closure of the repository, are analyzed. Also analyzed are the geochemical conditions and processes which may be involved in determining the radionuclide source term at the boundary of the waste package or engineered barrier system, and in controlling radionuclide transport through the geologic setting and release to the accessible environment. This letter report identifies: (1) the regulatory rationale for the geochemical issues, (2) the data and information needed to analyze the issues, (3) the methods, procedures, and approaches for obtaining the needed data and information, and (4) the precision and accuracy necessary, and the uncertainty acceptable, for the needed data and information.

3. GEOCHEMISTRY ISSUES

Geochemistry is the branch of geology that deals with the chemical composition of the rocks, minerals, and water in the earth's crust, and the chemical processes and resulting changes in composition that occur therein. Compliance with many of the regulatory guidelines, rules, and standards that pertain to site characterization and selection and construction, operation, and closure of a high-level waste repository will require knowledge of geochemical data and information. For example, the prediction of repository performance will be based on mathematical modeling, and geochemical data will be important input to the modeling activity. The technical issues included in this section address aspects of the geochemical environment of the repository site that may require resolution during various stages of the repository development and the licensing process between the NRC and the DOE.

3.1 WHAT ARE THE AMBIENT GEOCHEMICAL CONDITIONS AND PROCESSES IN THE GEOLOGIC SETTING?

Issue 3.1 addresses the ambient geochemical environment of the geologic setting, i.e., the conditions and processes existing prior to construction and operation activities which could alter the ambient environment. ("Geologic setting means the geologic, hydrologic, and geochemical systems of the region in which a geologic-repository operations area is or may be located"* [10 CFR Part 60.2; 10 CFR Part 960.2].) Knowledge of ambient geochemical conditions and processes will be an

*Quotation marks around a phrase or sentence indicates that it is a direct quote of the cited regulation.

important aspect of site characterization and selection. For example, guidelines and rules require knowledge of favorable conditions and of potentially adverse conditions. In addition, understanding of the ambient geochemical environment will provide a baseline for subsequent evaluation of the changes in geochemical conditions and processes that may occur as a result of construction, operation, and closure of the repository.

3.1.1 Regulatory Rationale

3.1.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR Part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

Implementation Guidelines - Information about the ambient geochemical conditions and processes will be needed to satisfy the siting provisions of the implementation guidelines detailed in Part 960.3-1. These siting provisions deal with the diversity of geohydrologic settings and rock types, regional distribution of sites, and steps for the identification of potentially acceptable sites. The evidence required to support nomination of a site for characterization is specified in Part 960.3-1-4-2, and the geochemical information required is detailed in Appendix IV, Section 960.4-2-2, Geochemistry. The geochemistry information should include:

- "Petrology of the rocks."

- "Mineralogy of the rocks and general characteristics of fracture fillings."
- "Geochemical and mechanical stability of the minerals under expected repository conditions."
- "General characteristics of the groundwater chemistry (e.g., reducing/oxidizing conditions and the principle ions that may affect the waste package or radionuclide behavior)."
- "Geochemical properties of minerals as related to radionuclide transport."

Portions of other parts of Appendix IV also define a need for ambient condition geochemical information. Under Appendix IV, Section 960.4-2-6, Dissolution, the required information should include:

- "The stratigraphy of the site, including rock units largely comprised of water-soluble minerals."
- "The extent of features indicative of dissolution within the geologic setting."

Additional ambient geochemical condition data needs are identified in some other sections of the guidelines. Data on fluid inclusions and gas content in the host rock are called for in Appendix IV, Section 960.5-2-9, Rock Characteristics. Pre-waste-emplacement groundwater conditions in the host rock that are chemically oxidizing are identified as a potentially adverse geochemistry condition [Part 960.4 2 2(c)(3)]. A natural resource postclosure favorable condition guideline [Part 960.4-2-8 1(b)(2)] addresses one aspect of ambient groundwater chemistry; groundwater with 10,000 parts per million or more of total dissolved solids along any path of likely radionuclide travel from the host rock to the accessible environment is considered a favorable condition.

Preclosure Guidelines - Preclosure guidelines are detailed in Part 960.5. These guidelines specify the factors to be evaluated in comparing sites on the basis of expected repository performance before closure. No geochemistry guidelines are specified, and little geochemical information may be needed to satisfy these preclosure guidelines. Most of the technical preclosure guidelines are related to mechanical aspects of the site rocks and hydrologic characteristics of the site.

Postclosure Guidelines - The postclosure guidelines [Part 960.4] are directed at the factors to be considered after repository closure, and as such they are addressed under Issues 3.3, 3.5, and 3.6. Some ambient condition geochemical information will be needed in the evaluation of these guidelines.

3.1.1.2 NRC Rules - The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

Siting criteria are defined in Part 60.122 that identify favorable and potentially adverse conditions that may exist at a site. The favorable conditions, together with the engineered barrier system, should be sufficient to provide reasonable assurance that the performance objectives will be met. Potentially adverse conditions, if present, must be investigated to demonstrate that the adverse condition does not compromise the performance of the geologic repository. Several of the favorable and potentially adverse conditions either explicitly or implicitly require knowledge of geochemical data and information.

The favorable conditions relevant to geochemistry issues are:

- Part 60.122(b)(1) - "The nature and rates of tectonic, hydrogeologic, geochemical, and geomorphic processes operating within the geologic setting during the Quaternary period, when projected, would not affect or would favorably affect the ability of the geologic repository to isolate the waste."
- Part 60.122(b)(3) - "Geochemical conditions that: (1) promote precipitation or sorption of radionuclides, (2) inhibit the formation of particulates, colloids, and inorganic or organic complexes that increase the mobility or radionuclides, or (3) inhibit the transport of radionuclides by particulates, colloids, and complexes."

- Part 60.122(b)(4) - "Mineral assemblages that, when subjected to anticipated thermal loading, will remain unaltered or alter to mineral assemblages having equal or increased capacity to inhibit radionuclide migration."

The potentially adverse conditions relevant to geochemistry issues are:

- Part 60.122(c)(7) - "Groundwater conditions in the host rock, including chemical composition, high ionic strength or ranges of Eh pH that could increase the solubility or chemical reactivity of the engineered barrier system."
- Part 60.122(c)(8) - "Geochemical processes that would reduce sorption of radionuclides, result in degradation of the rock strength, or adversely affect the engineered barrier system."
- Part 60.122(c)(20) - "Rock or groundwater conditions that would require complex engineering measures in the design and construction of the underground facility or in the sealing of boreholes and shafts."

3.1.1.3 EPA Standards - The EPA has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.1.2 Data and Information Needed to Analyze the Issue

3.1.2.1 Subsurface Temperature.

- Temperature vs depth in the site system

It is desirable to determine how ambient subsurface temperature affects: (1) groundwater composition, (2) the kinetics of rock-groundwater interactions, and, (3) the types and abundances of secondary minerals present in Yucca Mountain rocks. Knowledge of the effects of subsurface temperature on ambient geochemical conditions provides a baseline for predicting changes in geochemical conditions that will occur when a thermally disturbed zone develops during the postclosure period.

3.1.2.2 Lithostatic Pressure.

- Lithostatic pressure vs depth in the site system

Information on lithostatic pressure is required for predicting the mechanical properties of rocks in the structurally disturbed zone around the repository.

3.1.2.3 Hydrogeochemical Processes and Parameters.

- Patterns and rates of groundwater, aerosol, and gas flow in the unsaturated zone, and matrix potentials of unsaturated rocks adjacent to groundwater flow paths

It is important to identify groundwater flow paths in the unsaturated zone and to establish the role of fracture flow vs matrix flow in this zone. The faster the rate of flow of groundwater through the unsaturated zone (e.g., via fracture flow), the shorter the time available for rock-groundwater interactions and attendant changes in groundwater composition (e.g., increases in the concentrations of SiO_2 and dissolved salts).

- Hydrostatic pressure

Data on hydrostatic pressure (hydrostatic head) at depths beneath the static water table can be used to establish the velocities and directions of groundwater flow in the saturated zone.

- Effects of rock-groundwater interactions on the porosities and permeabilities of rocks along groundwater flow paths

Satisfactory predictions of the patterns and rates of groundwater flow and matrix diffusion of radionuclides require information on the porosities and permeabilities of the rocks along groundwater flow paths. Therefore, it would be useful to determine whether the porosities and permeabilities of rocks along groundwater flow paths have been affected significantly by rock-groundwater interactions. It is possible, for example, that deposition/growth of secondary minerals has decreased the porosities and permeabilities of the rocks immediately adjacent to groundwater flow paths.

3.1.2.4 Groundwater and Rock-Groundwater Interactions.

- Physicochemical properties of groundwater

The key physicochemical properties of groundwater are: (1) the major and minor element chemistry of solute material, (2) amounts and nature of dissolved gases, (3) the quantity and nature of organic material, speciation, pH, redox conditions, and (4) the quantities and compositions of suspended colloids and particulates. Information on these physicochemical properties is desirable for groundwaters in both the unsaturated and saturated zones beneath Yucca Mountain. It would be particularly useful to determine how the physicochemical properties of groundwater vary with host-rock composition, host-rock mineralogy, and groundwater flow rate. Finally, it would be of some interest to know whether Yucca Mountain groundwaters are saturated with any minerals that: (1) are currently observed in Yucca Mountain rocks, or (2) have the potential to form (precipitate) in these rocks.

- Kinetics of rock-groundwater interactions

It is advisable to obtain data on the kinetics of rock-groundwater interactions. In particular, it would be useful to have information on the kinetics of (1) dissolution of "reactive" minerals (e.g., tridymite) and (2) the precipitation of key sorptive phases (e.g., clinoptilolite and mordenite). Knowledge of the kinetics of rock-groundwater interactions under ambient conditions will provide a baseline for modeling the kinetics of rock-groundwater interactions in the thermally disturbed zone of the repository during the postclosure period.

3.1.2.5 Mineralogy

- Thermodynamic stabilities and reaction kinetics of the minerals in Yucca Mountain rocks

Information on the stability relations and reaction kinetics of the minerals in Yucca Mountain rocks under ambient conditions would facilitate satisfactory prediction of changes in mineral stability relations and reaction kinetics that will attend the development of a thermally disturbed zone in the site system during the postclosure period.

- Chemical compositions of the minerals in Yucca Mountain rocks

It would be useful to determine whether the compositions of the minerals in Yucca Mountain rocks vary with host-rock bulk composition and groundwater flow rate.

- Solubilities of the minerals in Yucca Mountain rocks

Information on the solubilities of individual minerals in Yucca Mountain rocks under ambient conditions would facilitate identification of the minerals which exert the greatest influence on groundwater composition.

3.1.2.6 Petrology.

- Bulk chemical compositions of rocks in the site system

It is possible that the chemical compositions of site groundwaters are influenced by both host-rock mineralogy and host-rock bulk composition. Therefore, information is needed on (1) the bulk chemical compositions of rocks in the site system and (2) the relationship, if any, between groundwater composition and host-rock bulk composition.

3.1.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.1.3.1 Subsurface Temperature

- downhole temperature probes
- measurements at surface during pump tests
- computer modeling (contouring) to produce 3-D temperature grid based on subsurface measurements

3.1.3.2 Lithostatic Pressure

- in situ stress/pressure measurements
- calculation based on density and thickness of rock sequence
- computer modeling (contouring) to produce 3-D pressure grid based on measured values

3.1.3.3 Hydrogeochemical Process and Parameters

- Patterns and rates of groundwater, aerosol, and gas flow in the unsaturated zone, and matric potentials of unsaturated rocks adjacent to the groundwater flow paths
  - hydrology subject

- Hydrostatic pressure
  - hydrology subject
- Effects of rock-groundwater interactions on the porosities and permeabilities of rocks along groundwater flow paths
  - rock-water interaction tests at various temperatures relevant to the repository host-rock system; models could be used but need to be checked against laboratory or field data
  - tests should be designed to investigate changes in porosity and permeability as dissolution and precipitation reactions occur in a flow-through system
  - parameters to be varied include: temperature, pressure, groundwater composition, time, groundwater flow rate, bulk-rock composition and mineralogy, initial porosity and permeability

3.1.3.4 Groundwater and Rock-Groundwater Interactions

- Physicochemical properties of groundwater
  - collect samples of groundwater from saturated zones using standard hydrologic techniques; samples should be preserved for analysis of cations, anions, silica, organics, and gases using standard methods
  - pH should be measured in the field at the time of collection using appropriate buffers and temperature compensation
  - collect samples from unsaturated zones; use centrifugation, filtration, and squeezing techniques to obtain samples; preserve for analysis; if necessary, these procedures should be performed under an inert atmosphere and appropriate temperature conditions

- methods for analysis of solution samples include:

  pH ... standard methods

  redox ... dissolved oxygen, aqueous redox couples, gas analysis, etc.

  major elements ... ICP, AA, IC, colorimetry

  minor elements ... ICP, AA, IC, colorimetry

  colloids ... filtration, centrifugation

  organics ... TOC, molecular weight analysis, GC/MS, etc.

  saturation index...geochemical models

- charge balance should be used as a criterion to evaluate the quality of any groundwater analysis and as a check that no major dissolved species was omitted

- Kinetics of Rock-Groundwater Interactions

  - laboratory tests required, complemented by study of natural mineral occurrences

  - low-temperature tests using minerals and rock from Yucca Mountain in aqueous solutions representative of groundwaters from saturated and unsaturated zone; tests should look at dissolution/precipitation of phases as function of time; data should be integrated into geochemical model so that results can be extrapolated to conditions and times somewhat outside the range of actual experiments

3.1.3.5 Mineralogy

- Thermodynamic stabilities and reaction kinetics of the minerals in Yucca Mountain rocks

  - rock/water interactions test (see 3.1.3.4)

- Chemical compositions of the minerals in Yucca Mountain rocks
    - XRD, EMP, SEM, TEM, XRF, INAA, etc.
- Solubilities of the minerals in Yucca Mountain rocks
    - use geochemical models and existing data bases to determine need for additional data (e.g., can the solubilities of minerals of interest be adequately predicted with current data)
    - determine solubilities experimentally for those phases that do not have adequate thermodynamic data

3.1.5.6 Petrology

- Bulk compositions of rocks in the site system
    - standard mineralogical and chemical techniques

3.1.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

TO BE COMPLETED BY AUGUST 31

3.2 WHAT ARE THE GEOCHEMICAL CONDITIONS OF THE ENGINEERING MATERIALS (PACKING, BACKFILL, AND SEALS) THAT MAY BE UTILIZED IN REPOSITORY CONSTRUCTION, OPERATION, AND CLOSURE?

Issue 3.2 addresses engineering materials placed in the repository. During characterization, construction, and operation of the repository site, bore holes, tunnels, shafts, drifts, etc. will be constructed. These man-made openings in the geologic site could compromise favorable site aspects and may represent potential pathways for rapid movement of groundwater and release of radionuclides to the accessible environment. Therefore, it is anticipated that various engineering materials will be employed during construction, operation, and closure of the repository to close or block these openings. Knowledge of the pre-emplacement geochemical conditions of these engineering materials will be needed to assess the potential impact of these materials on the geochemical environment of the site. Packing refers to materials that may be placed around and in contact with the waste canister; the packing, thus, is a component of the waste package. Backfill refers to materials that may be used to fill shafts, tunnels, drifts, etc. Seals refers to materials that may be used to seal boreholes or other openings to prevent movement of groundwater.

3.2.1 Regulatory Rationale

3.2.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR Part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

The DOE guidelines do not specifically mention engineering materials, such as packing, backfill, and seals, that may be used in the construction, operation, and closure of a repository. The guidelines are designed for application in the site selection process, and the guidelines specifically state that the possible isolation due to the use of engineered barriers is not to be relied upon to compensate for deficiencies in the geologic media [Part 960.3-1-5].

3.2.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

The NRC rules do not speak to the properties of engineering materials which may used in repository operation or closure. A few rules address the performance of seals, and these are analyzed under issues 3.4 and 3.5.

3.2.1.3 EPA Standards. The EPA has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.2.2 Data and Information Needed to Analyze the Issue

3.2.2.1 Initial Physicochemical Properties of Canister Metal

- Chemical composition

Important considerations in selecting the composition of canister metal are: (1) resistance to corrosion under oxidizing conditions, (2) potential effects of the metal on redox conditions in the vicinity of waste packages, (3) the effects of gamma radiation on the integrity of canister metal and on geochemical interactions between canister metal, packing material (if present), water-vapor-saturated air, and groundwater, and (4) resistance in typical groundwater chemistry.

3.2.2.2 Initial Physicochemical Properties of Packing Material (if Utilized)

The most recent reference design for waste packages in the proposed Yucca

Mountain repository (reference) does not include packing material. However, it is possible that future designs may include this material. Therefore, data and information needs concerning the physicochemical characteristics of packing material are discussed briefly below.

- Bulk chemical composition, mineralogy, porosity, and permeability

The bulk composition and mineralogy of packing material should be selected to maximize resistance to gamma radiation and hydrothermal alteration. Presumably, a highly stable packing material would be more likely to remain highly impervious to groundwater during the postclosure period.

3.2.2.3 Initial Physicochemical Properties of Backfill

- Bulk chemical composition, mineralogy, porosity, and permeability

Selection of backfill material should consider (1) the resistance of the material to low-temperature hydrothermal alteration and (2) the tendency of the material to increase the quantities of colloids and particulates suspended in site groundwaters.

3.2.2.4 Initial Physicochemical Properties of Seals

- Bulk chemical composition, types and compositions of solid phases, porosity, and permeability

Information on bulk composition, the types and compositions of solid phases, porosity, and permeability of the material used to construct seals (e.g., concrete?) would permit prediction of the geochemical performance of seals during the postclosure period. Data on the resistance of sealing material to low-temperature hydrothermal alteration would also be useful for performance assessment modeling.

3.2.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.2.3.1 Initial Physicochemical Properties of Canister Metal

- Chemical Composition
  - reported (usually) with material when received from vendor

3.2.3.2 Initial Physicochemical Properties of Packing Material (if utilized)

- Bulk chemical composition, mineralogy, porosity, and permeability
  - standard mineralogic and chemical techniques and hydrologic determinations

3.2.3.3 Initial Physicochemical Properties of Backfill

- Bulk Chemical Composition, mineralogy, porosity, and permeability
  - standard mineralogic and chemical techniques and hydrologic determinations

3.2.3.4 Initial Physicochemical Properties of Seals

- Bulk Chemical Composition, types and compositions of solid phases, porosity, and permeability
  - standard mineralogic and chemical techniques and hydrologic determinations

3.2.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

TO BE COMPLETED BY AUGUST 31

3.3 WHAT ARE THE CHANGES IN THE GEOCHEMICAL CONDITIONS AND PROCESSES IN THE DISTURBED ZONE THAT MAY OCCUR OVER TIME AS THE RESULT OF REPOSITORY CONSTRUCTION, OPERATION, AND CLOSURE, AND HOW MAY THESE CHANGES AFFECT THE ANTICIPATED REPOSITORY PERFORMANCE?

Issue 3.3 addresses the changes in the geochemical conditions and processes of the disturbed zone that may occur over time, and relates these changes to the prediction of repository performance. ("Disturbed zone means that portion of the controlled area, excluding shafts, whose physical or chemical properties are predicted to change as a result of underground facility construction or heat generated by the emplaced radioactive waste such that the resultant change of properties could have a significant effect on the performance of the geologic repository" [10 CFR Part 60.2; 10 CFR Part 960.2]). Ambient geochemical conditions and processes will be affected by numerous actions taken during characterization, selection, operation, and closure of the repository. For example, mining operations will introduce large volumes of air, and may alter groundwater flow patterns and affect mineral assemblages along release pathways. Also, the decay heat from the waste will alter the temperature profile of the setting after emplacement of waste and site closure. Such changes in geochemical conditions and processes could have significant effects on the anticipated repository performance and compliance with regulatory standards. Therefore, knowledge of these changes and their effects on the anticipated repository performance are important aspects of the modeling activity to demonstrate reasonable assurance or reasonable expectation of achieving the necessary degree of waste isolation.

3.3.1 Regulatory Rationale

3.3.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR Part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

Implementation Guidelines - One siting provision (Part 960.3-1) of the implementation guidelines addresses prediction of the affects of waste emplacement on the capability of the host rock to accommodate waste. Information on the thermal, mechanical, chemical, and radiation stresses induced by repository construction, operation, and closure is called for in Appendix IV, Section 960.4-2-3, Rock Characteristics.

Preclosure Guidelines - Preclosure guidelines are detailed in Part 960.5. These guidelines specify the factors to be evaluated in comparing sites on the basis of expected repository performance before closure. No geochemistry guidelines are specified and little geochemical information may be needed to satisfy these preclosure guidelines. Most of the technical preclosure guidelines are related to mechanical aspects of the site rocks and hydrologic characteristics of the site.

Postclosure Guidelines - The postclosure guidelines are listed in Part 960.4. These guidelines are to be considered in evaluating and comparing sites on the basis of expected repository performance after closure. ("Closure means final backfilling of the remaining open operational areas of the underground facility and boreholes after the termination of waste emplacement, culminating in the sealing of shafts" [Part 960.2].) Both system and technical guideline qualifying conditions are listed. A "qualifying condition" is a condition that must be satisfied for a site to be considered acceptable with respect to a specific guideline. The system qualifying condition [Part 960.4 1] states that the geologic setting at the site shall allow for physical separation of the radioactive waste from the accessible environment after closure in accordance with the requirements of 40 CFR Part 191, as implemented by the provisions of 10 CFR Part 60. Geochemistry postclosure technical guidelines are detailed in Part 960.4-2-2. The geochemical technical qualifying condition [Part 960.4-2-2(a)] states that the present and expected geochemical characteristics of a site shall be compatible with waste containment and isolation, considering the likely interactions among the radionuclides, host rock, and groundwater, and the characteristics and processes operating within the geologic setting shall permit compliance with the system postclosure guideline qualifying condition [Part 960.4 1].

The postclosure guidelines list favorable geochemistry conditions in Part 960.4-2-2(b). A "favorable condition" is defined as a condition that, though not necessary to qualify a site, is presumed, if present, to enhance confidence that the qualifying condition can be met. The favorable geochemistry conditions are:

- Part 960.4-2-2(b)(1) - "The rates and natures of the geochemical processes operating within the geologic setting during the Quaternary Period would, if continued into the future, not affect or would favorably affect the ability of the repository to isolate waste during the next 100,000 years."

- Part 960.4-2-2(b)(2) - "Geochemical conditions that promote the precipitation, diffusion into the rock matrix, or sorption of radionuclides; inhibit the formation of particulates, colloids, inorganic complexes, or organic complexes that increase the mobility of radionuclides; or inhibit the transport of radionuclides by particulates, colloids, or complexes."
- Part 960.4-2-2(b)(3) - "Mineral assemblages that, when subjected to expected repository conditions, would remain unaltered or would alter to mineral assemblages with equal or increases capability to retard radionuclide transport."
- Part 960.4-2-2(b)(4) - "A combination of expected geochemical conditions and a volumetric flow rate of water in the host rock that would allow less than 0.001 percent per year of the total radionuclide inventory in the repository at 1000 years to be dissolved."
- Part 960.4-2-2(b)(5) - "Any combination of geochemical and physical retardation processes that would decrease the predicted peak cumulative releases of radionuclides to the accessible environment by a factor of 10 as compared to those predicted on the basis of groundwater travel time without such retardation."

The postclosure guidelines list potentially adverse geochemistry conditions in Part 960.4-2-2(c). A "potentially adverse condition" is defined as a condition that is presumed to detract from expected system performance, but further evaluation, additional data, or mitigating factors may indicate that its effect on the system performance is acceptable. The potentially adverse conditions are:

- Part 960.4-2-2(c)(1) - "Groundwater conditions in the host rock that could affect the solubility or the chemical reactivity of the engineered barrier system to the extent that the expected repository performance could be compromised."
- Part 960.4-2-2(c)(2) - "Geochemical processes or conditions that could reduce the sorption of radionuclides or degrade rock strength."
- Part 960.4-2-2(c)(3) - "Pre-waste-emplacement groundwater conditions in the host rock that are chemically oxidizing."

Other geochemical information is called for in a postclosure guideline for a potentially adverse condition that deals with thermal aspects of rock characteristics. Part 960.4 2 3(c)(2) addresses the potential for such phenomena as the hydration or dehydration of mineral components, brine migration, or other physical, chemical, or radiation-related phenomena that could be expected to affect waste containment or isolation.

No disqualifying condition is identified under the postclosure guidelines for geochemistry [Part 960.4-2-2]. A "disqualifying condition" is defined as a condition that, if present at a site, would eliminate that site from further consideration.

3.3.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part

60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

The NRC rules do not directly address the changes which may occur as a result of construction, operation, and closure of a repository. Instead of considering the changes themselves, the rules are primarily performance oriented and, as such, the affect of changes are addressed in issue 3.5. Analysis of the expected performance will require knowledge of some chemical data and information. Rules which establish criteria for the waste package and its components given in Part 60.135 will specifically require knowledge of changes in ambient conditions and processes. A number of geochemistry and geochemistry-related factors are to be considered in the design of the waste packages. These include: solubility, oxidation/ reduction reactions, corrosion, hydriding, gas generation, thermal effects, radiolysis, radiation damage, radionuclide retardation, leaching, thermal loads, and synergistic interactions [Part 60.135(a)(2)].

3.3.1.3 EPA Standrds. The EPA has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.3.2 Data and Information Needed to Analyze the Issue

3.3.2.1 Preclosure Period

Effects of Repository Construction and Operation on Subsurface Temperature. Air ventilated through the shafts and drifts of the Yucca Mountain repository will lower wall rock temperatures and perhaps also decrease the temperatures of the rocks immediately above the repository horizon. The long-term effects of this thermal disturbance, if any, should be assessed.

Effects of Repository Construction and Operation on Hydrogeochemical Processes and Parameters

- Changes in the patterns and rates of groundwater, aerosol, and gas flow

It will be important to determine how the patterns and rates of groundwater, aerosol, and gas flow have been altered by repository siting and construction activities (exploratory drilling, shaft and drift construction, etc.) This information will be required for modeling changes in subsurface groundwater and gas flow that will begin to occur immediately after repository closure.

- Changes in the porosities, permeabilities, and matrix potentials of rocks near man-made openings

It is possible that construction and operation of the repository will have significant effects on the rocks in the structurally disturbed zone around the engineered facility. In particular, it is likely that the permeabilities and matrix potentials of these rocks will be altered by the drilling and blasting that will be required to construct this facility. Therefore, it would be informative to obtain information on the permeabilities and matrix potentials of the rocks in the structurally disturbed zone of the Yucca Mountain repository.

Effects of Repository Construction and Operation on Groundwater and Rock-Groundwater Interactions

- Changes in the physicochemical properties of groundwater

It will be important to determine how repository construction and operation activities affect key physicochemical properties of groundwaters (the major and minor element chemistry of solute material, amounts and composition of dissolved gases, the quantity and composition of organic material, speciation, pH, redox conditions, and the quantities and compositions of suspended colloids and particulates). This is particularly true for groundwaters that flow through the structurally disturbed rocks immediately adjacent to the engineered facility.

- Changes in rock-groundwater interactions along groundwater flow paths

It should be determined whether repository construction and operation activities result in any significant changes in rock-groundwater interactions along groundwater flow paths. This information will be required for modeling rock-groundwater interactions along groundwater flow paths during the postclosure period.

Effects of Repository Construction and Operation on Mineralogy

- Mineral assemblages and the chemical compositions of minerals

It should be determined whether repository construction and operation activities have any significant effects on the minerals in the rocks in the structurally disturbed zone of the Yucca Mountain repository.

3.3.2.2 Postclosure Period.

Changes in Subsurface Temperature During the Postclosure Period.

- Evolution of the thermally disturbed zone in the site system

Satisfactory repository performance-assessment modeling will require detailed information on the expansion and contraction of the thermally disturbed zone that will develop in the Yucca Mountain site system during the postclosure period.

Changes in Hydrogeochemical Processes and Parameters During the Postclosure Period -

- Changes in the patterns and rates of groundwater flow

Development of a disturbed zone in the Yucca Mountain repository site is apt to have major effects on the patterns and rates of groundwater flow in the unsaturated rocks adjacent to the engineered facility. Therefore, a satisfactory postclosure hydrologic model of groundwater and gas flow in the disturbed zone of the Yucca Mountain repository is required for defensible predictions of the performances of engineered barrier materials and site rocks.

- Changes in the porosities, permeabilities, and matrix potentials of rocks

During the postclosure period, it is possible that hydrothermal alteration will have significant effects on the porosities, permeabilities, and matrix potentials of the rocks adjacent to the engineered facility. This might occur, for example, if circulating groundwaters transport significant quantities of silica away from the comparatively hot rocks near waste packages toward cooler rocks above the repository horizon. Therefore, some consideration should be given to the effects of hydrothermal alteration on the hydrologic properties of the unsaturated rocks adjacent to the engineered facility.

Changes in the Physicochemical Properties of Groundwater and Rock-Groundwater Interactions -

- Changes in the physicochemical properties of groundwater during the postclosure period

Development of a disturbed zone in the Yucca Mountain repository site is apt to have major effects on the physicochemical properties of groundwaters that flow through the engineered facility and nearby rocks. In addition to increased rates of rock-groundwater interactions and attendant changes in groundwater composition caused by rising temperatures, it is possible that gamma radiation emanating from waste canisters will induce radiolytic reactions in the groundwaters that flow near waste packages. The latter possibility should be investigated because canister performance and radionuclide containment could be compromised if radiolytic reactions elevate the redox states of groundwaters in the very near field.

- Kinetics of rock-groundwater interactions

Increases in the temperatures of the rocks in the thermally disturbed zone of the Yucca Mountain repository site are likely to be accompanied by increased rates of rock-groundwater interactions. Therefore, it is important to determine how elevated temperatures will affect the kinetics of geochemical interactions between tuffaceous rocks and coexisting groundwaters.

Changes in Mineralogy During the Postclosure Period -

- Thermodynamic stabilities and reaction kinetics of the minerals in the thermally disturbed zone of the Yucca Mountain repository

Development of a disturbed zone in the Yucca Mountain site system will result in increases in temperature and changes in groundwater composition in the rocks adjacent to the engineered facility. Therefore, it should be determined how elevated temperatures and changes in groundwater composition will affect the thermodynamic stabilities and reaction kinetics of the minerals in the thermally disturbed zone of the Yucca Mountain repository.

- Chemical compositions of the minerals in the thermally disturbed zone of the Yucca Mountain repository

It should be determined whether low-temperature hydrothermal alteration will have any significant effects on the chemical compositions of the minerals in the thermally disturbed zone of the Yucca Mountain repository.

- Solubilities of the minerals in the thermally disturbed zone of the Yucca Mountain repository

Development of a disturbed zone in the Yucca Mountain site system will result in increases in temperature and changes in groundwater composition in the rocks adjacent to the engineered facility. Therefore, it should be determined how elevated temperatures and changes in groundwater composition affect the solubilities of the minerals in Yucca Mountain rocks.

- Radionuclide-sorption characteristics of the minerals in the thermally disturbed zone of the Yucca Mountain repository

It should be determined whether low-temperature hydrothermal alteration will have any significant effects on the radionuclide-sorption characteristics of the minerals in the thermally disturbed zone of the Yucca Mountain repository. Also, it should be determined whether or not low-temperature hydrothermal alteration changes the kinds and quantities of radionuclide-sorbing minerals in this zone.

Changes in Petrology During the Postclosure Period -

- Changes in the bulk chemical compositions of rocks in the site system

It should be determined whether rock-groundwater interactions (hydrothermal alteration) in the thermally disturbed zone of the repository will lead to any significant changes in the bulk chemical compositions of the rocks in this zone.

3.3.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.3.3.1 Preclosure Period

Effects of Repository Construction and Operation on Subsurface Temperature

- standard thermal models

Effects of Repository Construction and Operation on Hydrogeochemical Processes and Parameters

- Changes in patterns and rates of groundwater, aerosol, and gas flow
  - hydrology subject (likely to be one- and two-phase models supported by laboratory and field tests)
- Changes in the porosities, permeabilities, and matrix potentials of rocks near man-made openings
  - hydrology subject (models supported by laboratory and in situ tests likely approach)

Effects of Repository Construction and Operation on Groundwater and Rock-Groundwater Interactions

- Changes in physicochemical properties of groundwater
  - rock/water tests and in situ testing will be necessary to delineate potential changes; may be complemented by application of geochemical models
- Changes in rock/groundwater interactions along groundwater flow paths

  -see item immediately above

Effects of Repository Construction and Operation on Mineralogy

- Mineral assemblages and the chemical compositions of minerals
  - laboratory studies will be necessary to determine potential effects; in situ tests may be beneficial

3.3.3.2 Postclosure Period

Changes in Subsurface Temperature During Postclosure Period

- Evolution of the thermally disturbed zone in the site system
  - standard thermal models should be used

Changes in Hydrogeochemical Processes and Parameters During the Postclosure Period

- Changes in the patterns and rates of groundwater flow
  - hydrology subject
- Changes in the porosities, permeabilities, and matrix potentials of rocks
  - hydrology subject (likely to be models supported by laboratory and field tests)

Changes in the Physicochemical Properties of Groundwater and Rock-Groundwater Interactions

- Changes in the physicochemical properties of groundwater during the postclosure period
- Kinetics of rock-groundwater interactions
  - perform rock/water tests at appropriate temperature and pressure conditions to elucidate potential changes in the groundwater and solid phases present in the rocks; the atmosphere in these tests should be controlled so as to represent that present in the host-rock environment; some tests in the presence of radiation may be necessary

- tests should be complemented by geochemical modeling to the extent practicable

Changes in Mineralogy During the Postclosure Period

- Thermodynamic stabilities and reaction kinetics of the minerals in the thermally disturbed zone of the Yucca Mountain repository
- Chemical compositions of the minerals in the thermally disturbed zone of the Yucca Mountain repository
- Solubilities of the minerals in the thermally disturbed zone of the Yucca Mountain repository
  - perform rock/water tests at appropriate temperature and pressure conditions to elucidate potential changes in the groundwater and solid phases present in the rocks; the atmosphere in these tests should be controlled so as to represent that present in the host-rock environment; some tests in the presence of radiation may be necessary
  - tests should be complemented by geochemical modeling to the extent practicable

Radionuclide-sorption characteristics of the minerals in the thermally disturbed zone of the Yucca Mountain repository

- perform sorption tests on materials from the rock/water interactions tests (see section 3.6.3 for details on sorption data and methods)

Changes in Petrology During the Postclosure Period

- Changes in the bulk chemical compositions of rocks in the site system
  - perform rock/water tests at appropriate temperature and pressure conditions to elucidate potential changes in the groundwater and solid phases present in the rocks; the atmosphere in these tests should be controlled so as to represent that present in the

host-rock environment; some tests in the presence of radiation may be necessary

- tests should be complemented by geochemical modeling to the extent practicable

3.3.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

TO BE COMPLETED BY AUGUST 31

3.4 HOW WILL THE CHANGES IN THE GEOCHEMICAL CONDITIONS AND PROCESSES THAT MAY OCCUR OVER TIME AS A RESULT OF REPOSITORY CONSTRUCTION, OPERATION, AND CLOSURE AFFECT THE ANTICIPATED PERFORMANCE OF THE ENGINEERING MATERIALS (PACKING, BACKFILL, AND SEALS) UTILIZED IN THE REPOSITORY?

Issue 3.4 addresses the effects that changes in geochemical conditions and processes may have upon the anticipated performance of engineering materials placed in the repository during operation and closure. It is expected that engineering materials may be utilized to close man-made openings such as boreholes, tunnels, shafts, drifts, etc. which have been made in the geologic setting as a result of various site characterization, or repository construction and operation actions. Packing may be used in the annular space around the waste canister, backfill may be used to close tunnels and shafts, and seals may be used to prevent groundwater flow through boreholes, tunnels, shafts, etc. The anticipated performance of these materials may be dependent upon specific geochemical conditions or processes, and analysis of how changes in these conditions and processes affect the performance of these engineering materials is an important aspect of the predictive modeling of waste isolation by the repository.

3.4.1 Regulatory Rationale

3.4.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR Part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

The DOE guidelines do not specifically mention engineering materials, such as packing, backfill, and seals, that may be used in the construction, operation, and closure of a repository. The guidelines are designed for application in the site selection process, and the guidelines specifically state that the possible isolation due to the use of engineered barriers is not to be relied upon to compensate for deficiencies in the geologic media [Part 960.3-1-5].

3.4.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

Rules applicable to the seals for shafts and boreholes are given in Part 60.134. The general criterion states that seals shall be designed so that shafts and boreholes do not become pathways that compromise the ability of the geologic repository to meet the performance objectives of the period following permanent closure [Part 60.134(a)]. Also, the materials and placement of seals shall be selected so as to reduce radionuclide migration through existing pathways [Part 60.134(b)(2)].

3.4.1.3 EPA Standards. The EPA has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.4.2 Data and Information Needed to Analyze the Issue

3.4.2.1 Canister Metal.

Preclosure Period -

- Effects of prolonged exposure to decay heat, gamma radiation, and air

Information is needed on whether the integrity of canister metal will be affected significantly by prolonged heating, gamma irradiation, and exposure to air.

Postclosure Period -

- Effects of prolonged exposure to decay heat, gamma radiation, water-vapor-saturated air, and (late in the postclosure period) groundwater

Soon after repository closure, the waste canisters in the Yucca Mountain repository will be exposed to water-vapor-saturated air. Then, much later, after canister-surface temperatures have declined to less than 100°C, groundwater will come into direct contact with canister metal for extended periods of time before evaporating or flowing away from waste packages. These events, coupled with the effects of decay heat and gamma radiation, are expected to compromise waste containment by promoting canister corrosion. Therefore, information is needed on how the performance of canister metal is influenced by the geochemical conditions that develop near waste canisters during the postclosure period.

3.4.2.2 Packing Material (if present). The most recent reference design for waste packages in the proposed Yucca Mountain repository (reference) does not include packing material. However, it is possible that future designs may include this material. Therefore, discussion below describes data and information needs concerning possible changes in the physicochemical characteristics of packing material during the preclosure and postclosure periods.

Preclosure Period -

- Initial porosity and permeability. Effects of decay heat, gamma radiation, and short-term exposure to air

Satisfactory prediction of the performance of packing material is contingent upon obtaining information on how this material is affected by decay heat, gamma radiation, and exposure to air during the preclosure period.

Postclosure Period -

- Effects of prolonged exposure to decay heat, gamma radiation, water-vapor-saturated air, and (late in the postclosure period) groundwater

Modeling of the long-term (postclosure) performance of packing material requires data on the effects of exposure to decay heat, gamma radiation, water-vapor-saturated air, and groundwater. Geochemical events that could compromise the performance of packing material include localized boiling of groundwater (including deposition of the solute material in the groundwater) and hydrothermal alteration of the solid phases in the packing material. These events might result in significant changes in the porosity and permeability of packing material.

3.4.2.3 Backfill.

Preclosure Period -

- Effects of short-term exposure to air

It should be determined whether exposure to air during the preclosure period will have any significant effects on the long-term (postclosure) performance of backfill.

Postclosure Period -

- Effects of prolonged exposure to water-vapor-saturated air and throughflowing groundwater

It should be determined whether groundwater-backfill interactions during the postclosure period will have any significant effects on the compositions of throughflowing groundwaters and the quantities of colloids and particulates suspended in these groundwaters.

3.4.2.4 Seals.

Preclosure Period -

- Effects of exposure to air

Seals will be exposed to air for indefinite periods of time prior to emplacement in the repository. Therefore, it should be determined whether pre-emplacement exposure to air will have any significant effects on the long-term (postclosure) performance of repository seals.

Postclosure Period -

- Effects of prolonged exposure to water-vapor-saturated air and throughflowing groundwater

Satisfactory prediction of the performance of seals during the postclosure period requires information on how sealing material is affected by long-term exposure to water-vapor-saturated air and throughflowing groundwater.

3.4.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.4.3.1 Canister Metal

Preclosure Period

- Effects of prolonged exposure to decay heat, gamma radiation, and air

  - corrosion subject

Postclosure Period

- Effects of prolonged exposure to decay heat, gamma radiation, water-vapor-saturated air, and (late in the postclosure) groundwater

  - corrosion subject, but the conditions of testing should be defined by tests discussed in section 3.3.3

3.4.3.2 Packing Material (if present)

Preclosure Period

- Initial porosity and permeability. Effects of decay heat, gamma radiation, and short-term exposure to air

  - laboratory tests should be used to alter the material and then standard methods for porosity and permeability should be applied.

Postclosure Period

- Effects of prolonged exposure to decay heat, gamma radiation, water-vapor-saturated air, and (late in the postclosure period) groundwater)

  - laboratory tests under appropriate geochemical conditions should be used to alter the material and then the porosity and permeability determined via standard methods

3.4.3.3 Backfill

Preclosure Period

- Effects of short-term exposure to air

  - laboratory tests using relevant geochemical conditions should be performed; any changes in the properties of the backfill material should be assessed using standard mineralogical and chemical techniques; changes in porosity and permeability should also be determined

Postclosure Period

- Effects of prolonged exposure to water-vapor- saturated air and throughflowing groundwater

  - see preclosure discussion

3.4.3.4 Seals

Preclosure Period

- Effects of short-term exposure to air

  - see 3.4.3.3

Postclosure Period

- Effects of prolonged exposure to water-vapor- saturated air, and throughflowing groundwater

  - see 3.4.3.3

3.4.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

(TO BE COMPLETED BY AUGUST 31)

3.5 WHAT ARE THE GEOCHEMICAL CONDITIONS AND PROCESSES THAT MAY AFFECT THE RADIONUCLIDE SOURCE TERM AT THE BOUNDARIES OF (1) THE WASTE PACKAGES DURING THE CONTAINMENT PERIOD AND (2) FROM THE ENGINEERED BARRIER SYSTEM IN THE POST CONTAINMENT PERIOD, AND HOW MAY THE ANTICIPATED REPOSITORY PERFORMANCE BE INFLUENCED?

The geochemical conditions and processes that may affect the radionuclide source term or release rate are analyzed in issue 3.5. The time after repository closure is divided into two periods that have different performance objectives. During the containment period of not less than 300 years or more than 1000 years, NRC rules require that containment of waste by the waste package must be substantially complete. In the post-containment period after 300 to 1000 years, the allowable release rate of radionuclides from the engineered barrier system is specified by NRC rules. Mathematical modeling will be utilized to predict the source term or release rate of radionuclides during these post-closure periods, and geochemical data and information will be important input required by the modeling activity. An understanding of the relevant geochemical conditions and processes, and their influence on the source term, may be crucial to demonstrating reasonable assurance of anticipated repository compliance with the relevant regulations.

3.5.1 Regulatory Rationale

3.5.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR Part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

The postclosure system guideline qualifying condition [Part 960.4-1(a)] states that the geologic setting at the site shall allow for the physical separation of radioactive waste from the accessible environment after closure in accordance with the requirements of 40 CFR Part 191, Subpart B, as implemented by the provisions of 10 CFR 60. As discussed below (Section 3.5.1.2), provisions of 10 CFR 60 deal with the permissible radionuclide release rate, or source term, in the postclosure period. Geochemical data will be needed to support modeling of the source term. Other than that qualifying condition, the source term at the waste package is not specifically addressed in the DOE guidelines.

3.5.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

Performance Objectives. The performance objectives first set general objectives for the performance of the repository operations area through closure [Part 60.111(a)], for the option of retrievability of waste at up to 50 years after the start of waste emplacement [Part 60.111(b)], and for the overall performance of the repository after closure to assure that radioactive material releases shall conform to the EPA standards [Part 60.112].

The general provisions for the performance of particular barriers after closure differentiate between performance during the period when radiation and thermal conditions are dominated by decay, i.e., the period of containment, and for small fractional releases over long times, i.e., the post-containment period [Part 60.113(a)]. A subpart of the general provision specifically addresses the need for analysis of groundwater information for disposal in the saturated zone [Part 60.113(a)(i)(B)].

The performance of particular barriers after closure are detailed in Part 60.113. The rules specified in Part 60.113 are important to the analysis of geochemical issues because they establish the repository performance that must result from the action of particular barriers at specified times after closure. The containment of waste within the waste package must be substantially complete for the period of containment [Part 60.113(a)(1)(i)(A)]. ("Waste package is defined to mean the waste form and any containers, shielding, packing and other absorbent materials immediately surrounding an individual waste container" [Part 60.2].) "Substantially complete" is not described in the definitions [Part 60.2]. The period of containment is required to be not less than 300 years nor more than 1000 years following permanent closure [Part 60.113(a)(1)(ii)(A)]. ("Permanent closure means final backfilling of the underground facility and the sealing of shafts and boreholes" [Part 60.2].) Computer modeling will be necessary to predict conformance with these rules, and geochemical data and information will be important input to the modeling activity.

Following the containment period, the release rate of any radionuclide from the engineered barrier system shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure of the repository [Part 60.113(a)(1)(ii)(B)]. ("Engineered barrier system is defined to mean the waste packages and the underground facility" [Part 60.2].) It is important to note that as a result of this wording, the rule specifies release rates after the containment period from the overall engineered facility, and not from the individual waste packages as in the containment period. An exception to the one in 100,000 release rate rule is provided for any radionuclide which is released at a rate less than 0.1% of the calculated total release rate. The calculated total release rate shall be taken to be one part in 100,000 per year of the inventory of radioactive waste that remains after 1000 years of decay after original emplacement [Part 60.113(a)(1)(11)(B)]. Note that 1000 years after original emplacement may be a slightly shorter time than 1000 years after permanent closure.

Computer modeling will be necessary to predict conformance with these rules, and geochemical data and information will be important input to the modeling activity.

Part 60.113 also contains a clause that allows the NRC to approve or specify some other release rate, containment period, etc., on a case-by-case basis [Part 60.113(b)]. Various types of information are to be taken into account in such a performance variance, including the geochemical characteristics of the host rock, surrounding strata, and groundwater [Part 60.113(b)(3)].

Design Criteria for the Waste Package. Rules which establish criteria for the waste package and its components are given in Part 60.135. A number of geochemistry and geochemistry-related factors are to be considered in the design of the waste packages. These include: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, radiolysis, radiation damage, radionuclide retardation, leaching, thermal loads, and synergistic interactions [Part 60.135(a)(2)].

3.5.1.3 EPA Standards. The NRC has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or election of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyze only under Issue 3.6.

3.5.2 Data and Information Needs

3.5.2.1 Containment Period. Information on the geochemical processes and conditions that affect corrosion and radionuclide release (post-containment) is essential to the success of performance assessments for engineered barrier systems. The nature of these processes and conditions is needed as a function of time (through 1000 years for the containment period) so that corrosion and source term models can account for changing conditions and processes. Ranges and distributions of parameter values are required for geochemical conditions essential to the performance of the engineered barrier system. The nature, extent, and probability of occurrence is needed for the key processes. This probabilistic information is needed to support performance assessment calculations addressing the reliability of the engineered barrier system. The processes and conditions that may be active in and around the engineered barrier system are discussed below.

- Temperature: Temperature effects corrosion processes, geochemical conditions, and radionuclide release from engineered barrier system. Information on temperature is needed as a function of time and distance within the engineered barrier system.
- Pressure: Pressure is a fundamental parameter that is most important to the failure of the waste package canister. Pressure effects impact other processes and conditions, but not as importantly as temperature. Information is needed on both lithostatic and hydrostatic pressures as a function of time and distance within the engineered barrier system.
- Groundwater Chemistry: The groundwater chemistry effects corrosion

processes, geochemical conditions, and radionuclide release from engineered barrier system. Parameters that must be quantified as a function of time include:

- redox, pH, major and minor element chemistry
- organics, colloids, particulates
- should consider effects of temperature, pressure, gamma-radiation, and rock/water/barrier interactions for all of the above

• Solids: Natural and engineered materials, as well as the presence of their alteration products, will impact the overall performance of the engineered barrier system. It will be important to quantify the corrosion of metallic canisters, the alteration of packing material (changing hydrologic-isolation performance and sorption characteristics), the thermal effects on the physical nature of the waste form, etc. The nature of these solids at the time of failure and beyond is needed so that release models can account for any processes that promote or inhibit the release and transport of radionuclides. Important parameters which must be quantified over time include:

  - waste form, canister material, packing, crushed rock, and host rock
  - should consider effects from temperature, pressure, gamma-radiation, and rock/water/barrier interactions
  - information should include: (1) bulk composition, (2) mineralogy surface characterization, and nature of failure for barriers (i.e, type and extent of canister corrosion)

• Hydrologic Setting: Information is needed on the flow field around the engineered barrier system prior to the time of failure and beyond so that geochemical conditions that affect corrosion and radionuclide release can be quantified. Important parameters which must be quantified over time include:

- porosity and permeability for each barrier (component) that may affect the flow field (e.g., host rock, packing, canister, waste form). General information on the ambient and post-closure flow-field will also be required.

3.5.2.2 Post-Containment Period. Information on the geochemical processes and conditions that affect radionuclide release is essential to performance assessments of engineered barrier systems. The nature of these processes and conditions is needed as a function of time (from time of failure through 10,000 years) so that source term models can account for changing conditions and processes. The source term models will be used to evaluate compliance with the slow-release criterion and to provide a source term for transport models addressing the 10,000 year cumulative release criterion. Ranges and distributions of parameter values are required for geochemical conditions essential to the performance of the engineered barrier system. The nature, extent, and probability of occurrence is needed for the key processes. This probabilistic information is needed to support performance assessment calculations addressing the reliability of the engineered barrier system. The processes and conditions that may be active in and around the engineered barrier system are discussed below.

- Temperature: Temperature effects geochemical conditions that control the release of radionuclides from the engineered barrier system.

Information is needed as a function of time and distance within the engineered barrier system.

- Pressure: Pressure is a fundamental parameter that is most important to the failure of the waste package canister. It impacts other processes and conditions, but not as importantly as temperature. Information is needed on both lithostatic and hydrostatic pressures as a function of time and distance within the engineered barrier system.
- Groundwater Chemistry: Groundwater chemistry effects geochemical conditions thus radionuclide release from engineered barrier system. Important parameters which must be quantified over time include:
  - redox, pH, major and minor element chemistry
  - organics, colloids, particulates
  - should consider effects of temperature, pressure, gamma-radiation, alpha-radiation, and rock/water/barrier interactions for all of the above
- Solids: Natural and engineered materials, as well as the presence of their alteration products will impact the overall performance of the engineered barrier system. It will be important to quantify the corrosion of metallic canisters, the alteration of packing material (changing hydrologic-isolation performance and sorption characteristics), the thermal effects on the physical nature of the waste form, etc. The nature of these solids at the time of failure and beyond is needed so that release models can account for any processes that promote or inhibit the release and transport of radionuclides. Important parameters which must be quantified over

time include:

- waste form, canister material, packing, crushed rock, and host rock
- should consider effects from temperature, pressure, gamma-radiation, and rock/water/barrier interactions
- information should include: (1) bulk composition, (2) mineralogy, surface characterization, and nature of failure for barriers (i.e, type and extent of canister corrosion)

- Hydrologic Setting: Information is needed on the flow field around the engineered barrier system prior to the time of failure and beyond so that geochemical conditions that affect corrosion and radionuclide release can be quantified. Important parameters which must be quantified over time include:

  - porosity and permeability for each barrier (component) that may affect the flow field (e.g., host rock, packing, canister, waste form)

  General information on the ambient and post-closure flow-field will also be required.

- Source-Term Parameters: The following parameters are typically used in source models. The parameters can be used to provide a concentration and rate of mass transfer at various points away from the waste packages. The information can be used to homogenize release across the entire repository also. Information on reactions within the engineered barrier system is important because these reactions can slow down or speed up release of radionuclides from the waste form.

Information on the speciation of radionuclide-bearing solutions is not essential to source models, but is essential for performing acceptable sorption tests so that far-field transport models will be reliable.

- aqueous concentration of all key radionuclides at waste form interface (e.g., "solubility," steady-state concentration, dissolution rates)
- diffusion coefficients for all key radionuclides in solutions of interest
- "retardation" reactions that may occur within the engineered barrier system (e.g., ion-exchange, ppt, redox, etc.)
- speciation of solutions likely to be released from the engineered barrier system
- vapor/aerosol transport of radionuclides
- should consider effects of kinetics, groundwater flow rate, temperature, pressure, radiation (alpha and gamma), and rock/water/barrier interactions

3.5.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.5.3.1 Containment Period

- Temperature
  - standard thermal models should be adequate to predict temperatures around the waste package
- Pressure
  - see 3.1.3.2 for determination of hydrostatic and lithostatic pressure

- thermomechanical models will be needed to predict the stress fields around the waste package for analysis of canister failure

- Groundwater Chemistry
  - see 3.3.3 and 3.3.4
- Solids
  - see 3.3.3 and 3.3.4
- Hydrologic Setting
  - hydrology subject

3.5.3.2 Post-containment Period

- Temperature, Pressure, Groundwater Chemistry, Solids, Hydrologic Setting
  - see 3.5.3.1
- Source Term Parameters
  - concentrations of radionuclides:

Waste/barrier/water/rock interactions tests will be required to establish concentrations for all the important radionuclides. The tests should be conducted using relevant geochemical conditions and materials. Standard methods for solution and solid analyses should be employed. Criteria to establish that "steady state" has been reached should be developed. To the extent practicable, an understanding of the reactions involved should be established so that extrapolations of the data can be accomplished with geochemical models.

Parameters to be considered in the design of the experiments include: time, groundwater flow rate, temperature, pressure, and radiation.

- diffusion coefficents:

  Diffusion coefficients should be determined using standard methods for multicomponent systems. Conditions of chemistry, temperature, etc. should be based upon results of tests and modeling as outlined in sections 3.3.3 and 3.4.3

- retardation reactions within engineered system:

  Sorption tests should be completed using relevant geochemical conditions (see 3.6.3 for details of sorption procedures).

- speciation of solutions:

  To the extent practicable, the speciation of radionuclides in the resulting solutions should be determined. This determination could be acommplished using standard speciation techniques or geochemical models. As an alternative, the solutions from these tests could be directly used in sorption tests designed to assess the far-field transport of radionuclides.

- vapor/aerosol transport of radionuclides:

  A combination of laboratory tests, field tests, and modeling could be used to quantify the role of vapor/aerosol transport. The tests should utilize relevant geochemical conditions and materials.

3.5.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

(TO BE COMPLETED BY AUGUST 31)

3.6 WHAT GEOCHEMICAL CONDITIONS AND PROCESSES AFFECT THE TRANSPORT OF MOBILIZED RADIONUCLIDES THROUGH THE GEOLOGIC SETTING AND THE RELEASE RADIONUCLIDES TO THE ACCESSIBLE ENVIRONMENT AFTER DISPOSAL, AND HOW MAY THE ANTICIPATED REPOSITORY PERFORMANCE BE INFLUENCED?

Issue 3.6 analyzes the geochemical conditions and processes that affect the transport of mobilized radionuclides through the geologic setting to the accessible environment. Issue 3.5 analyzed the source term or release rate of radionuclides from the waste packages or the engineered facility which results in mobilized radionuclides. The NRC rules analyzed in issue 3.5 differentiate between two time periods after disposal; the period of substantially complete containment of radionuclides by the individual waste packages (not less than 300 years or more than 1000 years), and the post-containment period where the allowable radionuclide release rate from the engineered facility is one part in 10,000 of the 1000 year inventory of each radionuclides. The EPA standards analyzed in this issue do not address those arbitrary time periods in the NRC rules, but instead deal with releases to the accessible environment for times up to 10,000 years after disposal.

The rate of movement or retardation of mobilized radionuclides in groundwater are subject to various geochemical conditions and processes during transport through the geologic setting. The EPA standards establish the cumulative release limits for 10,000 years after disposal for various radionuclides to the accessible environment. Mathematical modeling will be employed to demonstrate anticipated compliance with these standards, and geochemical data and information will be important input for the modeling activity.

3.6.1 Regulatory Rationale

3.6.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

The postclosure system guideline qualifying condition [Part 960.4-1(a)] states that the geologic setting at the site shall allow for the physical separation of radioactive waste from the accessible environment after closure in accordance with the requirements of 40 CFR Part 191, Subpart B, as implemented by the provisions of 10 CFR 60. As discussed below (Section 3.5.1.3), provisions of 40 CFR 191 deal with the cumulative release rates of radionuclides to the accessible environment. Geochemical data will be needed to support modeling of these release rates. Other that qualifying condition, the transport and release of radionuclides to the accessible environment is not specifically addressed in the DOE guidelines.

3.6.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10],

although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

The NRC rules do not directly address releases of radionuclides to the accessible environment. The overall system performance objective states that the performance of the setting and the engineered barrier systems shall be designed so as to assure that releases of radionuclides to the accessible environment conform to standards established by the EPA [Part 60.122].

3.6.1.3 EPA Standards. The EPA has promulgated standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository.

The EPA standards are designed to limit the exposure of members of the public from the management and storage of spent fuel, or high-level or transuranic wastes [Part 191, Subpart A], and sets requirements for disposal of these materials [Part 191, Subpart B]. The primary standards for disposal are long-term containment requirements that limit projected releases of radioactivity to the accessible environment for 10,000 years after disposal. ("Accessible environment means: (1) the atmosphere; (2) land surfaces; (3) surface waters; (4) oceans, and (5) all of the lithosphere that is beyond the controlled area" [Part 191.12(k)]. "Controlled area means: (1) a surface location, to be identified by passive institutional controls, that encompasses no more than 100 square kilometers and extends horizontally no more than five kilometers in any direction from the outer boundary of the original location of the radioactive wastes in a disposal system, and (2) the subsurface underlying such a surface location" [Part 191.12(g)].) Assurance requirements are specified to provide confidence that the containment requirements will be met. Finally, a set of groundwater protection requirements are also established for the period of 1000 years after disposal.

Containment Requirements. The containment requirements are detailed in Part 191.13. The standard states that the disposal systems (any combination of engineered and geologic barriers) shall provide a reasonable expectation that the cumulative releases of radionuclides to the accessible environment shall: (1) have a likelihood of less than one chance in 10 of exceeding the quantities calculated according to Table 1, Appendix A, and (2) have a likelihood of less than one chance in 1000 of exceeding 10 times the quantities calculated according to Table 1, Appendix A [Part 191.13(a)]. This standard is the primary containment requirement which details the required performance of a repository for 10,000 years, and, as such, it must be carefully and thoroughly analyzed.

Table 1. Release limits for containment requirements[a]

(Cumulative releases to the accessible environment for 10,000 years after disposal)

Radionuclide	Release Limit per 1000 MTHM[b] or other unit of waste (see notes) (Ci)
Americium-241 or -243	100
Carbon-14	100
Cesium-135 or -137	1,000
Iodine-129	100
Neptunium-237	100
Plutonium-238, -239, -240, or -242	100
Radium-226	100
Strontium-90	1,000
Technetium-99	10,000
Thorium-230 or -232	10
Tin-126	1,000
Uranium-233, -234, -235, -236, -238	100
Any other alpha-emitting radionuclide with a half-life greater than 20 years	100
Any other radionuclide with a half-life greater than 20 years that does not emit alpha particles	1,000

[a]From 40 CFR 191, Appendix A.
[b]MTHM - metric ton of heavy metal, i.e., uranium, plutonium, etc.

"Reasonable expectation" is not specifically defined, however the concept is dealt with under Part 191.13(b) which states: "Performance assessments need not provide complete assurance that the requirements of 191.13(a) will be met. Because of the long time period involved and the nature of the events and processes of interest, there will inevitably be substantial uncertainties in projecting disposal system performance. Proof of the future performance of a disposal system is not to be had in the ordinary sense of the word in situations that deal with much shorter time frames. Instead, what is required is a reasonable expectation, on the basis of the record before the implementing agency, that compliance with 191.13(a) will be achieved." Guidance for the implementation of the containment requirement is included in Part 191, Appendix B. The guidance states that compliance will involve predicting the likelihood of events and processes that may disturb the disposal system. In making these predictions, the guidance states that it will be appropriate to make use of rather complex computational models, analytical theories, and prevalent expert judgment relative to the numerical predictions. The guidance suggests that numerical predictions may be supplemented with qualitative judgments.

The release limits which apply to the containment requirement are detailed in Part 191, Appendix A, Table 1. Cumulative release limits for 10,000 years after disposal are given for a number of individual radionuclides and groups of radionuclides. ("Disposal means permanent isolation of spent nuclear fuel or radioactive waste from the accessible environment with no intent of recovery, whether or not such isolation permits the recovery of such fuel or waste. For example, disposal of waste in a mined geologic repository occurs when all of the shafts to the repository are backfilled and sealed" [Part 191.02(1)].) Thus, the EPA term "disposal" is equivalent to the NRC term "permanent closure". Table 1 of Appendix A to Part 191 is repeated below. A number of extended footnotes to Table 1 define units of waste and explain the application of the release limits to different types of waste [Part 191, Appendix A]. These footnotes will have to be carefully examined and considered in order to apply the radionuclide release limits in Table 1 to the analysis of the anticipated performance of a given repository.

Considering the relevant standard [Part 191.13] and associated guidance, it seems apparent that resolution of Issue 3.6 may require considerable data and information descriptive of the geochemical conditions and processes which affect radionuclide migration through the geologic setting. As a consequence of the containment requirement of cumulative release limits for individual radionuclides and the associated release limit units for specific types of waste and disposal systems, the performance required of the geologic setting at a specific repository will be dependent on the mixture and types of wastes which are assumed to be emplaced. Thus, analysis of the affect of geochemical or other geotechnical conditions and processes with regard to Issue 3.6 can not be made independent of the assumed waste content of the repository upon closure. This need for waste data in addition to data and information for the geochemical conditions and processes may appreciably complicate the quantitative analysis of Issue 3.6.

Groundwater Protection Requirements. The groundwater protection requirements [Part 191.16] are designed to insure that, for 1000 years after disposal, any water drawn from a special source shall not exceed the EPA interim drinking water standards as specified in 40 CFR Part 141. (A special source of groundwater includes waters that are within the controlled area, are supplying drinking water for thousands of people, and are irreplaceable in that no alternative drinking water is available to that populace [Part 191.12(o)].) Application of this standard seems to require that, for 1000 years after repository closure, very little to essentially no radioactivity may be released from the waste into groundwaters. This standard may be consistent with an NRC rule requiring a containment period of substantially complete containment of waste by the waste package for 1000 years after closure, but seems potentially inconsistent with a shorter period of time for the NRC containment period, for example such as 300 years.

3.6.2 Data and Information Needed to Analyze the Issue

The data and information needed to analyze Issue 3.6 is primarily associated with the EPA 10,000-year-cumulative-radionuclide-containment-requirement standard [40 CFR Part 191.13(a)]. In this evaluation, the radionuclides are assumed to be transported by flowing groundwater, either as solutes, colloids, or particulates. Geochemical processes are important in controlling the mobility of radionuclides in the geologic setting and the rate of release of radionuclides to the accessible environment, and important processes are discussed in the following section. The action of these processes in the various hydrogeologic regimes at Yucca Mountain are then considered in a subsequent section. The mathematical modeling methodology used to predict the cumulative radionuclide release rates is yet to be established. In this situation, it may not be possible to anticipate all the data and information needed to predict the effects of radionuclide dissolution and precipitation processes in the modeling activity. Interaction between the modelers and the geochemists should be an ongoing activity to insure that requisite data and information becomes available in a timely manner.

3.6.2.1 Geochemical Processes. The three predominant geochemical processes affecting radionuclide mobility are: (1) dissolution/ precipitation, (2) sorption, and (3) matrix diffusion. These processes are analyzed in the following subsections. Filtration also could be an effective waste isolation process in some cases, and filtration is briefly discussed. Time exerts an important influence on the cumulative release of radionuclides, and time also is discussed in a following subsection.

Radionuclide Dissolution/Precipitation Processes. The combined effects of dissolution and precipitation processes control the solubility or concentration of a given radionuclide in solution. The solution is assumed to be groundwater, either of a composition initially present at the site before repository construction and waste disposal, or of a composition altered due to repository construction and waste disposal operations. Solubility refers to the saturated solution concentration of a radionuclide species in equilibrium with a solid phase containing that radionuclide. If sufficient thermodynamic data are available descriptive of the solid, solution species, groundwater parameters, and thermal evolution of the repository, the solubility may be calculated. Concentration refers to the actual concentration of a given radionuclide in solution as determined by some analytical method. The concentration may be less than the solubility of that radionuclide if the solution is not saturated,or may be greater if supersaturation has occurred. The saturated solution concentration is equivalent to the solubility value for a given solid phase. An apparent concentration limit is the maximum amount of a radionuclide which can be obtained in a solution by experimental methods, and may be equivalent to the solubility value.

The types of data or information needed to analyze the effects of the dissolution/precipitation processes on the transport and release of radionuclides include: (1) groundwater composition, (2) groundwater redox conditions and pH, (3) mineral assemblages and host rock composition along the release pathway, (4) radionuclide solution species, (5) radionuclide particle and colloidal forms, both real and pseudo, (6) dissolution and precipitation reaction kinetics, and (7) radiolysis reactions. Knowledge of the mathematical modeling methodology will also be needed to ensure that the geochemical data obtained is appropriate for the modeling activity.

The groundwater composition, and parameters such as pH and redox conditions, play an important role in controlling the solubility of radionuclide species, and information about these groundwater aspects will be needed. Groundwater composition and parameters may change, relative to initial values, due to reactions with waste package components. Thermal effects resulting from decay heat after closure which could accelerate slow reactions and/or initiate new rock/groundwater reactions will also need to be evaluated. Therefore, the compositions and parameters of all groundwaters in the radionuclide release pathway will need to be considered. Information concerning ions present in the groundwater which could form complexes with radionuclides and thereby increase solubility or hinder sorption will be particularly important.

It is anticipated that radionuclide release through the geologic setting may follow discrete pathways. Therefore, knowledge of the mineral assemblages along the potential release pathways will be needed to understand the rock/groundwater reactions and the radionuclide and/or groundwater component dissolution//precipitation reactions which may occur during migration. Some radionuclides show large differences in solubility or apparent concentration limit with relatively minor changes in groundwater composition and parameters.

Radiolysis reactions in the vicinity of the waste packages may alter the groundwater composition and conditions, or the radionuclide species, as a result of reactions with products of radiolysis of water and air such as hydrogen peroxide or nitric acid. An understanding of radiolytic effects may be needed, particularly during the first few hundred years when fission product decay generates strong gamma radiation which can penetrate the canister and interact with groundwater in the vicinity of the canister. Alpha radiolysis reactions with groundwater would become important only after canister failure when groundwater comes into contact with the waste form, because alpha radiation will be strongly adsorbed by the canister. Alpha radiolysis reactions could play a significant role in establishing the actinide-element speciation in solution due to the presence of multiple valences and species of actinide elements formed from radiolytic reactions. Therefore, long-term modeling of actinide release rates may require some information regarding alpha radiolysis reactions.

Sorption Process. Radionuclides migrating in groundwater may be retarded, relative to the groundwater flow rate, due to sorption onto solids present in the geologic setting. Sorption refers to any set of geochemical processes that result in the binding of radionuclides to geologic solids. Terms such as ion exchange, adsorption, or chemisorption are sometimes used to identify specific sorption processes. However, sorption reactions are difficult to characterize, and we have chosen not to attempt to discuss subclasses of sorption reactions. The types of data and information needed to analyze the effects of sorption on the transport and release of radionuclides include: (1) mineral assemblages along the release pathway, (2) groundwater composition, (3) groundwater redox conditions and pH, (4) radionuclide species, (5) sorption/desorption kinetics, (6) sorption competition between radionuclides and groundwater species, and (7) sorption isotherms. Knowledge of the controlling reactions and minerals and of the mathematical modeling methodology will be needed to ensure that the sorption data obtained is appropriate for the modeling activity.

Radionuclides may be present in groundwater in a number of forms that, in turn, may display different mobilities. Solute species, whether ionic or non-ionic, may be expected to move at the groundwater flow rate unless sorption reactions bind these species to minerals or rock phases adjacent to the release pathway. Because many sorption reactions have at least some aspects of ion exchange phenomena, it may be anticipated that cationic species of radionuclides may be much more strongly sorbed and retarded than anionic or non-ionic species. Therefore, knowledge of the speciation of radionuclide solutes may be considered necessary in order to predict sorption retardation.

Colloidal or particulate forms of radionuclides may exhibit mobilities different from solute forms. Colloidal radionuclides, either as true colloids of radionuclide solid phases or as pseudocolloids of radionuclides carried by sorption or coprecipitation with groundwater or mineral colloids, may be retarded relative to groundwater flow by sorption or filtration processes. Thus, knowledge of the various colloids and particulates which may be present in migrating groundwater, as well as the degree of crystallinity or particle size of radionuclide precipitates, will be necessary information.

Radionuclide speciation is controlled by groundwater composition and parameters such as pH and redox condition. Thus, as for radionuclide solubility, knowledge of these groundwater aspects will be necessary. Radionuclides species may have greatly different sorption coefficients for different minerals. Knowledge of the mineral assemblages along the release pathway and measurement of radionuclide sorption ratios with representative or actual minerals and groundwaters will be essential to supply sorption data supportive of retardation modeling activities.

Retardation of solutes due to the sorption process is a multi-stage process that represents the sum of many sorption and desorption reaction steps between the solid and solution phases. To accurately model the degree of retardation anticipated for a given radionuclide, it may be necessary to measure both the steady-state sorption and desorption ratios and the rates of the sorption and desorption reactions. These measurements must be made under conditions representative of the mineral assemblages and groundwater compositions to be encountered along release pathways. The exact data needed will, in part, depend on the migration modeling methodology selected. Competition between different radionuclides, or between radionuclides and groundwater constituents, may affect the sorption and desorption ratios for some radionuclides. Also, the effect of radionuclide concentration on the sorption and desorption ratios must be considered. To deal with these aspects of radionuclide sorption, sorption and desorption isotherms may need to be constructed for various groundwater compositions and radionuclide mixtures. Again, the exact data needed will, in part, depend on the migration modeling methodology selected.

Matrix Diffusion Process. Matrix diffusion is defined as the aqueous diffusion of molecules or ions from a water-filled fracture into the groundwater contained in adjacent porous rock. Prediction of the rates of migration of radionuclides through the host rock and the quantities of radionuclides that may be released from a repository will require knowledge of the retardation that may result from matrix diffusion of radionuclides. A number of variables affect matrix diffusion in rock media. These include: (1) fracture aperture, (2) groundwater velocity through fractures, (3) solute concentration gradients between fractures and matrix, (4) degree of matrix saturation with groundwater, (5) matrix porosity, and (6) effective diffusion coefficients for diffusing species. Quantitative knowledge of all these parameters may be needed to accurately assess the possible radionuclide retardation which may result from matrix diffusion. In general, the effects of matrix diffusion are enhanced by: (1) narrow fracture apertures, (2) slow rates of groundwater flow, (3) steep solute concentration gradients between fractures and matrix, (4) complete saturation of the matrix by groundwater, (5) high matrix porosity, and (6) large diffusion coefficients for diffusing species. When fractured rocks have a high sorptive capacity for dissolved species in groundwater, matrix diffusion is largely restricted to comparatively small volumes of rocks adjacent to fractures. Because there are so many different and highly variable physicochemical factors that can influence the nature and extent of matrix diffusion of radionuclides as a retardation mechanism, it may be difficult to predict the significance of matrix diffusion for the anticipated repository performance.

Filtration Process. Filtration is the process whereby particulates are trapped during movement through a porous medium. Filtration may only be a significant radionuclide retardation process in the event that radionuclides can be transported through the geologic setting as adsorbed species on the surface of naturally-occurring particles or particles resulting from waste package/groundwater reactions.

Time. Several aspects of time are important in controlling the release of radionuclides to the accessible environment. Although time is not, strictly speaking, a geochemical process, the effects of time are inextricably intertwined with the geochemical processes discussed above. The important aspects of time with respect to radionuclide transport and release are: (1) radionuclide half-life, (2) groundwater travel time, and (3) regulatory times.

Radionuclides are temporally unstable. Thus, the decay constant (half-life) of the radionuclide, the length of time for travel from the engineered facility to the accessible environment (the product of groundwater travel time and the retardation factor), and the regulatory requirement or repository performance time-frame being modeled all can have a major effect on the cumulative radionuclide releases. Data and information about these temporal aspects of radionuclide transport will be needed. If, for example, the half-life of a given radionuclide is short compared to the travel time to the environment from the engineered facility, then releases of that radionuclide may be inherently minor or negligible. In that case, accurate data and information on the geochemical behavior of this radionuclide may be of minor significance in the release modeling activity.

3.6.2.2 Repository-Depth Zones at Yucca Mountain. Because groundwater transport is the most credible mechanism that could lead to transport of mobilized radionuclides and release of radionuclides to the accessible environment, the discussion of data and information needs is subdivided below into subsections corresponding to the major repository-depth zones at Yucca Mountain.

Unsaturated Zone Above the Reference Repository Horizon. Rock/groundwater reactions in this zone affect the compositions of groundwaters that may flow toward the waste packages. Fracture flow of groundwater is more likely in this zone than in subjacent zones. Because groundwater flows down through this zone on its way to subjacent zones, it is unlikely that this zone will ever become contaminated with radionuclides. It is possible, but unlikely, that some quantities of radionuclides could enter this zone by upward movement of radionuclide-bearing vapors or aerosols.

Data and information will be needed descriptive of the composition(s) and parameter(s) of groundwater which may be expected to enter the engineered facility from above and contact the waste packages. To help extend these predictions over the 10,000-year regulatory time-frame, knowledge of the mineral assemblages along groundwater flow paths in this zone and how the composition and conditions of groundwater may change with time will also be needed.

At the present time, little is known about the possibility of vapor or aerosol transport of radionuclides in the engineered facility of the geologic setting. If, in the future, information develops that such transport could be significant, then the question of radionuclide transport upward into the unsaturated zone above the repository may need to be addressed.

Unsaturated Zone at the Reference Repository Horizon. Data and information needs for this zone include the quantities of hydrous minerals in the rocks adjacent to the engineered facility and the mechanical properties of these rocks. The smectite-rich layer at the top of the basal vitrophyre of the Topopah Spring member may provide significant radionuclide sorption capacity and thus may afford a first line of defense against radionuclide transport through the geologic setting.

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Geochemical data and information will be needed to describe the radionuclide dissolution/precipitation processes and sorption process that could be effective in this zone. Radionuclides released from the engineered facility by groundwater may be limited in concentration due to solubility constraints, and radionuclide concentrations may need to be measured or calculated for this unsaturated zone. In addition, radionuclides may be sorbed onto rocks of this zone. In particular, sorption of cations by smectite often exhibits high sorption ratios. Thus, measurements of smectite sorptive behavior will be needed if the DOE chooses to take credit for sorption in this zone as a radionuclide release barrier. Methods of measuring and modeling sorption in an unsaturated environment could need to be developed. The effect of possible radiolysis reactions on the groundwater composition and radionuclide speciation should be considered in this zone in the vicinity of the waste packages. The presence or absence of colloidal or particulate forms of radionuclides also needs to be confirmed.

Unsaturated Zone Below the Reference Repository Horizon. Zeolite-rich rocks in this zone are potentially important barriers to radionuclide migration because they may provide significant radionuclide sorption capability. The rates of downward flow of groundwater may decrease significantly in this zone because unwelded tuff is more porous and permeable than the welded Topopah Spring tuff in the superjacent zone and less fracture flow may occur. This is the first zone in which significant matrix diffusion of radionuclides could occur.

Data and information will be needed which is descriptive of the radionuclide dissolution/precipitation processes, sorption process, and matrix diffusion process. The groundwater composition and conditions may change due to contact with clinoptilolite and mordenite, and the changes in groundwater parameters could affect the radionuclide solubility. Sorption of radionuclides by these zeolitic minerals likely will be different than with the sorptive clay minerals in the superjacent zone. Because sorption in this zone could be a major radionuclide release barrier, measurement of radionuclide sorptive behavior likely will be needed. Methods of measuring and modeling sorption in an unsaturated environment may need to be developed. Some measurements of matrix diffusion may also be needed if the DOE chooses to take credit for this process as a radionuclide release barrier in this zone.

Saturated Zone. The volume of groundwater is much higher in this zone than in superjacent zones. Also, the rates of downward movement of groundwater may be greatly diminished in this zone while rates of lateral movement may be greatly enhanced. Ingressing radionuclide-bearing groundwaters would be highly diluted by mixing with the radionuclide-free groundwaters that flow through this zone. Significant matrix diffusion of radionuclides is much more likely in this zone than in the superjacent unsaturated zones. This zone may contain regions in which redox conditions are more reducing than in the highly-oxidized rocks in superjacent zones. Also, smectite-rich and zeolite-rich regions of this zone may provide significant radionuclide sorption capability. As in the cases of the superjacent zones, data and information will be needed to describe the radionuclide solubility or concentration, for the sorption and desorption reactions, and for matrix diffusion. Existing batch contact and column chromatographic experimental and modeling methodology may be adequate to describe sorption in the saturated zone. The groundwater composition and conditions may change in this zone due to dilution and reaction with a different mineral assemblage. Information descriptive of the groundwater composition and conditions and their affects on radionuclide solubility and sorption reactions likely will be needed. Matrix diffusion of radionuclides could be an important radionuclide release barrier in this zone and data on matrix diffusion will be needed. Considering the total effect of these geochemical processes, it is possible that this zone could provide appreciable retardation for mobilized radionuclides and, thus, data and information needed to evaluate retardation will be important.

3.6.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.6.3.1 Radionuclide Dissolution/Precipitation Processes

(1) groundwater composition - analysis of samples of *in situ* groundwaters and groundwaters altered by thermal/radiolysis effects due to emplacement of waste and engineered facility components; chemical analyses for major and minor components by ICP, AA, NAA, and wet chemical methods for both inorganic and organic constituents

(2) groundwater redox condition and pH - analysis of samples of *in situ* groundwaters and groundwaters altered by thermal/radiolysis effects due to emplacement of waste and engineered facilitycomponents; pH measurement with standard electrodes, Eh measurement with platinum

electrode, estimation of system Eh by measurement of element couples [e.g., Fe(II)/Fe(III)] in solution, calculation of system Eh from data on mineral assemblages

(3) mineral assemblages and host rock compositions along the release pathway - recovery of samples from drill holes and exploratory shaft; analysis by physical methods (XRD, SEM) and chemical methods to identify major and minor minerals; important to do cross section of samples to identify minerals in direct contact with flowing water

(4) radionuclide solution species - identify solution speciation (valence, complexation, hydrolysis) by spectroscopic, lacer-induced photoelectron spectroscopic, and electrochemical methods of radionuclides dissolved in *in situ* groundwaters and groundwaters altered by thermal/radiolysis effects due to emplacement of waste and engineered facility components

(5) radionuclide particle and colloid forms - identify particles/ colloids in *in situ* groundwaters, groundwaters altered by thermal/radiolysis effects due to emplacement of waste or engineered facility components by Debye light scattering, sequential filtration techniques; chemical analysis of recoverable particles/colloids

(6) dissolution and precipitation reaction kinetics - measurement of both major and minor mineral/host rock components, and radionuclide concentrations in *in situ* groundwaters and groundwaters altered by thermal/radiolysis effects due to emplacement of waste and engineered facility components; AA, NAA, ICP, wet chemical, and spectroscopic methods

(7) radiolysis reactions - chemical analysis for radiolysis reaction products of groundwater such as H_2O_2, organic acids, and changes in radionuclide speciation

3.6.3.2 Sorption Process

(1) mineral assemblages along the release pathway - see above

(2) groundwater composition - see above

(3) groundwater redox condition and Eh - see above

(4) radionuclide species - see above

(5) sorption/desorption kinetics - both batch contact and column chromatographic methodology should be employed to study radionuclide sorption and desorption reactions as a function of time; test conditions and parameters should span the ranges anticipated in the repository over time; groundwaters and substrates should include those expected in the engineered facility and along the release pathway

(6) sorption competition between radionuclides and groundwater species - sorption/desorption kinetic studies (see 5 above) should have an expanded test matrix to include variable concentration of groundwater species

(7) sorption isotherms - batch contact methodology should be employed with the test matrix (see 5 above) including various concentrations of radionuclides to allow construction of sorption isotherms

3.6.3.3 Matrix Diffusion Process

(1) fracture aperture - both the average and range of fracture

apertures should be measured by down-hole and direct methods from the exploratory shaft

(2) groundwater velocity through fractures - measured from the exploratory shaft

(3) solute concentration gradients between fractures and matrix - measured in laboratory experiments

(4) degree of matrix saturation with groundwater - measured by heating and weighing samples recovered from air-sparged drill holes and from the exploratory shaft

(5) matrix porosity - measured by BET and mercury infusion techniques on samples recovered from drill holes and from the exploratory shaft

(6) effective diffusion coefficients for diffusing species - radionuclides allowed to diffuse from groundwater samples into wafers or pieces of matrix recovered from drill holes and exploratory shaft; depth of penetration determined as a function of time

3.6.3.4 Filtration Process

Removal-from-solution of radionuclides onto colloidal or dispersed particulates by flow through matrix samples recovered from drill holes and exploratory shaft

3.6.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

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LETTER REPORT

TITLE: Geochemistry Issues for the Hanford Site Candidate High-Level Waste Repository

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SUMMARY

This letter report describes geochemical technical issues (Section 3, Geochemistry Issues, in the Nuclear Regulatory Commission (NRC) hierarchy of geotechnical issues) for the Hanford Site candidate high-level waste repository being characterized by the Department of Energy (DOE). These issues are derived from DOE guidelines, NRC rules, and Environmental Protection Agency (EPA) standards that explicitly or implicitly indicate a need for geochemical information relevant to (1) site characterization and selection, and (2) construction, operation, and closure of a repository. The issues are focused on geochemical conditions and processes that have a direct bearing on repository containment requirements and performance objectives, and the issues are related to repository performance at various stages in time. The ambient geochemical conditions and processes, and the changes in these geochemical conditions and processes which may occur over

time as a result of construction, operations, and closure of the repository, are analyzed. Also analyzed are the geochemical conditions and processes which may be involved in determining the radionuclide source term at the boundary of the waste packages or engineered barrier system, and in controlling radionuclide transport through the geologic setting and release of radioactivity to the accessible environment. This letter report identifies: (1) the regulatory rationale for the geochemical issues, (2) the data and information needed to analyze the issues, (3) the methods, procedures, and approaches for obtaining the needed data and information, and (4) the precision and accuracy necessary, and the uncertainty acceptable, for the needed data and information.

3. GEOCHEMISTRY ISSUES

Geochemistry is the branch of geology that deals with the chemical composition of the rocks, minerals, and water in the earth's crust, and the chemical processes and resulting changes in composition that occur therein. Compliance with many of the regulatory guidelines, rules, and standards that pertain to (1) site characterization and selection, and (2) construction, operation, and closure of a high-level waste repository will require knowledge of geochemical data and information. For example, the prediction of repository performance will be based on mathematical modeling, and geochemical data will be important input to the modeling activity. The technical issues included in this section address aspects of the geochemical environment of the repository site that may require resolution during various stages of the repository development and licensing process between the NRC and the DOE.

3.1 WHAT ARE THE AMBIENT GEOCHEMICAL CONDITIONS AND PROCESSES IN THE GEOLOGIC SETTING?

Issue 3.1 addresses the ambient geochemical environment of the geologic setting, i.e., the conditions and processes existing prior to construction and operation activities which could alter the ambient environment. ("Geologic setting means the geologic, hydrologic, and geochemical systems of the region in which a geologic-repository operations area is or may be located"* [10 CFR Part 60.2; 10 CFR Part 960.2].)

*Quotation marks around a phrase or sentence indicates that it is a direct quote of the cited regulation.

Knowledge of ambient geochemical conditions and processes will be an important aspect of site characterization and selection. For example, guidelines and rules require knowledge of favorable or of potentially adverse conditions. In addition, understanding of the ambient geochemical environment will provide a baseline for subsequent evaluation of the changes in geochemical conditions and processes that may occur as a result of construction, operation, and closure of the repository.

3.1.1 Regulatory Rationale

3.1.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR Part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

Implementation Guidelines - Information about the ambient geochemical conditions and processes will be needed to satisfy the siting provisions of the implementation guidelines detailed in Part 960.3-1. These siting provisions deal with the diversity of geohydrologic settings and rock types, regional distribution of sites, and steps for the identification of potentially acceptable sites. The evidence required to support nomination of a site for characterization is specified in Part 960.3-1-4-2, and the geochemical information required is detailed in Appendix IV, Section 960.4-2-2, Geochemistry. The geochemistry information should include:

- "Petrology of the rocks."
- " Mineralogy of the rocks and general characteristics of fracture fillings."
- "Geochemical and mechanical stability of the minerals under expected repository conditions."
- "General characteristics of the groundwater chemistry (e.g., reducing/oxidizing conditions and the principle ions that may affect the waste package or radionuclide behavior)."
- "Geochemical properties of minerals as related to radionuclide transport."

Portions of other parts of Appendix IV also define a need for ambient condition geochemical information. Under Appendix IV, Section 960.4-2-6, Dissolution, the required information should include:

- "The stratigraphy of the site, including rock units largely comprised of water-soluble minerals."
- "The extent of features indicative of dissolution within the geologic setting."

Additional ambient geochemical condition data needs are identified in some other sections of the guidelines. Data on fluid inclusions and gas content in the host rock are called for in Appendix IV, Section 960.5-2-9, Rock Characteristics. Pre-waste-emplacement groundwater conditions in the host rock that are chemically oxidizing are identified as a potentially adverse geochemistry condition [Part 960.4-2-2(c)(3)]. A natural resource postclosure favorable condition guideline [Part 960.4-2-8-1(b)(2)] addresses one aspect of ambient groundwater chemistry; groundwater with 10,000 parts per million or more of total dissolved solids along any path of likely radionuclide travel from the host rock to the accessible environment is considered a favorable condition.

Preclosure Guidelines - Preclosure guidelines are detailed in Part 960.5. These guidelines specify the factors to be evaluated in comparing sites on the basis of expected repository performance before closure. No geochemistry guidelines are specified and little geochemical information may be needed to satisfy these preclosure guidelines. Most of the technical preclosure guidelines are related to mechanical aspects of the site rocks and hydrologic characteristics of the site.

Postclosure Guidelines - The postclosure guidelines [Part 960.4] are directed at the factors to be considered after repository closure, and as such they are addressed under Issues 3.3, 3.5, and 3.6. Some ambient condition geochemical information will be needed in the evaluation of these guidelines.

3.1.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

Siting criteria are defined in Part 60.122 that identify favorable and potentially adverse conditions that may exist at a site. The favorable conditions, together with the engineered barrier system, should be sufficient to provide reasonable assurance that the performance objectives will be met. Potentially adverse conditions, if present, must be investigated to demonstrate that the adverse condition does not compromise the performance of the geologic repository. Several of the favorable and potentially adverse conditions either explicitly or implicitly require knowledge of geochemical data and information.

The favorable conditions relevant to geochemistry issues are:

- Part 60.122(b)(1) - "The nature and rates of tectonic, hydrogeologic, geochemical, and geomorphic processes operating within the geologic setting during the Quaternary period, when projected, would not affect or would favorably affect the ability of the geologic repository to isolate the waste."
- Part 60.122(b)(3) - "Geochemical conditions that: (1) promote precipitation or sorption of radionuclides, (2) inhibit the formation of particulates, colloids, and inorganic or organic

complexes that increase the mobility or radionuclides, or (3) inhibit the transport of radionuclides by particulates, colloids, and complexes."

- Part 60.122(b)(4) - "Mineral assemblages that, when subjected to anticipated thermal loading, will remain unaltered or alter to mineral assemblages having equal or increased capacity to inhibit radionuclide migration."

The potentially adverse conditions relevant to geochemistry issues are:

- Part 60.122(c)(7) - "Groundwater conditions in the host rock, including chemical composition, high ionic strength or ranges of Eh-pH that could increase the solubility or chemical reactivity of the engineered barrier system."
- Part 60.122(c)(8) - "Geochemical processes that would reduce sorption of radionuclides, result in degradation of the rock strength, or adversely affect the engineered barrier system."
- Part 60.122(c)(20) - "Rock or groundwater conditions that would require complex engineering measures in the design and construction of the underground facility or in the sealing of boreholes and shafts."

3.1.1.3 EPA Standards. The EPA has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.1.2 Data and Information Needed to Analyze the Issue

3.1.2.1 Subsurface Temperature.

- Temperature vs depth in the site system

It is desirable to determine how ambient subsurface temperature affects: (1) groundwater composition, (2) the kinetics of rock-groundwater interactions, and, (3) the types and abundances of secondary minerals present in Hanford Site rocks. Knowledge of the effects of subsurface temperature on ambient geochemical conditions provides a baseline for predicting changes in geochemical conditions that will occur when a thermally disturbed zone develops during the postclosure period.

3.1.2.2 Lithostatic Pressure.

- Lithostatic pressure vs depth in the site system

Information on lithostatic pressure is required for predicting the mechanical properties of rocks in the structurally disturbed zone around the repository.

- Hydrostatic pressure

Data on hydrostatic pressure (hydrostatic head) at depths beneath the static water table can be used to establish the velocities and directions of groundwater flow in the saturated zone.

- Effects of rock-groundwater interactions on the porosities and permeabilities of rocks along groundwater flow paths

Satisfactory predictions of the patterns and rates of groundwater flow and matrix diffusion of radionuclides require information on the porosities and permeabilities of the rocks along groundwater flow paths. Therefore, it would be useful to determine whether the porosities and permeabilities of rocks along groundwater flow paths have been affected significantly by rock-groundwater interactions. It is possible, for example, that deposition/growth of secondary minerals has decreased the porosities and permeabilities of the rocks immediately adjacent to groundwater flow paths.

3.1.2.3 Groundwater and Rock-Groundwater Interactions.

- Physicochemical properties of groundwater

The key physicochemical properties of groundwater are: (1) the major and minor element chemistry of solute material, pH, and redox conditions, (2) amounts and nature of dissolved gases, (3) the quantity and characteristics organic material, (4) the quantities and compositions of suspended colloids and particulates. It would be particularly useful to determine how the physicochemical properties of groundwater vary with host-rock composition, host-rock mineralogy, and groundwater flow rate. Finally, it would be of some interest to know whether Hanford Site groundwaters are saturated with any minerals that: (1) are currently observed in Hanford site rocks, or (2) have the potential to form (precipitate) in these rocks.

• Kinetics of rock-groundwater interactions

It is advisable to obtain data on the kinetics of rock-groundwater interactions. In particular, it would be useful to have information on the kinetics of (1) dissolution of "reactive" minerals and mesostasis and (2) the precipitation of key sorptive phases (e.g., zeolites and amorphous iron-manganese oxides). Knowledge of the kinetics of rock-groundwater interactions under ambient conditions will provide a baseline for modeling the kinetics of rock-groundwater interactions in the thermally disturbed zone of the repository during the postclosure period.

3.1.2.4 Mineralogy

• Thermodynamic stabilities and reaction kinetics of the minerals in Hanford Site rocks

Information on the stability relations and reaction kinetics of the minerals in Hanford Site rocks under ambient conditions would facilitate satisfactory prediction of changes in mineral stability relations and reaction kinetics that will attend the development of a thermally disturbed zone in the site system during the postclosure period.

• Chemical compositions of the minerals phases in Hanford Site rocks

It would be useful to determine whether the compositions of the minerals and mesostasis, as well we the degree of crystallinity of the mesostasis in Hanford Site rocks vary with host-rock bulk composition and groundwater flow rate.

- Solubilities of the minerals in Hanford Site rocks

Information on the solubilities of individual minerals in Hanford Site rocks under ambient conditions would facilitate identification of the minerals which exert the greatest influence on groundwater composition.

- Radionuclide-sorption characteristics of the minerals in Hanford Site rocks

Information on the radionuclide-sorption characteristics of individual mesostasis in Hanford Site rocks under ambient conditions would provide a baseline for modeling sorption of radionuclides in the thermally disturbed zone and far field of the Hanford Site repository during the postclosure period.

3.1.2.6 Petrology.

- Bulk chemical compositions of rocks in the site system

It is possible that the chemical compositions of site groundwaters are influenced by both host-rock mineralogy (e.g. percent crystallinity as well as minerals present) and host-rock bulk composition. Therefore, information is needed on (1) the bulk chemical compositions of rocks in the site system, (2) chemical composition of mesostasis, and (3) the relationship, if any, between groundwater composition and host-rock bulk composition.

3.1.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.1.3.1 Subsurface Temperature.

- downhole temperature probes
- measurements at surface during pump tests
- computer modeling (contouring) to produce 3-D temperature grid based on subsurface measurements

3.1.3.2 Lithostatic Pressure.

- in situ stress/pressure measurements
- calculation based on density and thickness of rock sequence
- computer modeling (contouring) to produce 3-D pressure grid based on measured values

3.1.3.3 Hydrogeochemical Processes and Parameters.

- Hydrostatic pressure
    - hydrology subject
- Effects of rock-groundwater interactions on the porosities and permeabilities of rocks along groundwater flow paths
    - rock-water interaction tests at various temperatures relevant to the repository host-rock system; models could be used but need to be checked against laboratory or field data
    - tests should be designed to investigate changes in porosity and permeability as dissolution and precipitation reactions occur in a flow-through system
    - parameters to be varied include: temperature, pressure, groundwater composition, time, groundwater flow rate,

bulk-rock composition and mineralogy, initial porosity and permeability

3.1.3.4 Groundwater and Rock-Groundwater Interactions.

- Physicochemical properties of groundwater

  - collect samples of groundwater from saturated zones using standard hydrologic techniques; samples should be preserved for analysis of cations, anions, silica, organics, and gases using standard methods
  - pH should be measured in the field at the time of collection using appropriate buffers and temperature compensation
  - methods for analysis of solution samples include:

pH ...	standard methods
redox ...	dissolved oxygen, aqueous redox couples, gas analysis, etc.
major elements ...	ICP, AA, IC, colorimetry
minor elements ...	ICP, AA, IC, colorimetry
colloids ...	filtration, centrifugation
organics ...	TOC, molecular weight analysis, GC/MS, etc.
saturation index...	geochemical models

  - charge balance should be used as a criterion to evaluate the quality of any groundwater analysis and as a check that no major dissolved species was omitted

- Kinetics of Rock-Groundwater Interactions
  - laboratory tests required, complemented by study of natural mineral occurrences
  - low-temperature tests using minerals and rock from Hanford in aqueous solutions representative of groundwaters; tests should look at dissolution/precipitation of phases as function of time; data should be integrated into geochemical model so that results can be extrapolated to conditions and times somewhat outside the range of actual experiments

3.1.3.5 Mineralogy.

- Thermodynamic stabilities and reaction kinetics of the minerals in Hanford Site rocks
  - rock/water interactions test (see 3.1.3.4)
- Chemical compositions of the minerals in Hanford Site rocks
  - XRD, EMP, SEM, TEM, XRF, INAA, etc.
- Solubilities of the minerals in Hanford Site rocks
  - use geochemical models and existing data bases to determine need for additional data (e.g., can the solubilities of minerals of interest be adequately predicted with current data)
  - determine solubilities experimentally for those phases that do not have adequate thermodynamic data

- Radionuclide-sorption characteristics of the minerals in Hanford Site rocks

  - see Section 3.6.3

3.1.3.6 Petrology

- Bulk chemical compositions of rocks in the site system

  - standard mineralogical and chemical techniques

3.1.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

(TO BE COMPLETED BY SEPTEMBER 30)

3.2 WHAT ARE THE GEOCHEMICAL CONDITIONS OF THE ENGINEERING MATERIALS (PACKING, BACKFILL, AND SEALS) THAT MAY BE UTILIZED IN REPOSITORY CONSTRUCTION, OPERATION, AND CLOSURE?

Issue 3.2 addresses engineering materials placed in the repository. During characterization, construction, and operation of the repository site, boreholes, tunnels, shafts, drifts, etc. will be constructed. These man-made openings in the geologic site could compromise favorable site aspects and may represent potential pathways for rapid movement of groundwater and release of radionuclides to the accessible environment. Therefore, it is anticipated that various engineering materials will be employed during construction, operation, and closure of the repository to close or block these openings. Knowledge of the pre-emplacement geochemical conditions of these engineering materials will be needed to assess the potential impact of these materials on the geochemical environment of the site. Packing refers to materials that may be placed around and in contact with the waste canister; the packing, thus, is a component of the waste package. Backfill refers to materials that may be used to fill shafts, tunnels, drifts, etc. Seals refers to materials that may be used to seal boreholes or other openings to prevent movement of groundwater.

3.2.1 Regulatory Rationale

3.2.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR Part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

The DOE guidelines do not specifically mention engineering materials, such as packing, backfill, and seals, that may be used in the construction, operation, and closure of a repository. The guidelines are designed for application in the site selection process, and the guidelines specifically state that the possible isolation due to the use of engineered barriers is not to be relied upon to compensate for deficiencies in the geologic media [Part 960.3-1-5].

3.2.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10],

although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

The NRC rules do not speak to the properties of engineering materials which may used in repository operation or closure. A few rules address the performance of seals, and these are analyzed under issues 3.4 and 3.5.

3.2.1.3 EPA Standards. The EPA has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.2.2 Data and Information Needed to Analyze the Issue

3.2.2.1 Initial Physicochemical Properties of Canister Metal

- Chemical composition

Important considerations in selecting the composition of canister metal are: (1) resistance to corrosion under oxidizing conditions, (2) potential effects of the metal on redox conditions in the vicinity of waste packages, (3) the effects of gamma radiation on the integrity of canister metal and on geochemical interactions between canister metal, packing material (if present), and groundwater. While the reference waste package design has not been finalized for the Hanford Site, it is possible that future designs may include this material. Therefore, data and information needs concerning the physicochemical characteristics of packing material are discussed briefly below.

- Bulk chemical composition, mineralogy, porosity, and permeability

The bulk composition and mineralogy of packing material should be selected to maximize resistance to gamma radiation and hydrothermal alteration. Presumably, a highly stable packing material would be more likely to remain highly impervious to groundwater during the postclosure period.

3.2.2.3 Initial Physicochemical Properties of Backfill

- Bulk chemical composition, mineralogy, porosity, and permeability

Selection of backfill material should consider (1) the resistance of the material to hydrothermal alteration, (2) the tendency of the material to increase the quantities of colloids and particulates suspended in site groundwaters, and (3) minimization of adverse changes to the groundwater composition.

3.2.2.4 Initial Physicochemical Properties of Seals

- Bulk chemical composition, types and compositions of solid phases, porosity, and permeability

Information on bulk composition, the types and compositions of solid phases, porosity, and permeability of the material used to construct seals (e.g. concrete?) would permit prediction of the geochemical performance of seals during the postclosure period. Data on the resistance of sealing material to low-temperature hydrothermal alteration would also be useful for performance assessment modeling.

3.2.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.2.3.1 Initial Physicochemical Properties of Canister Metal

- Chemical Composition
  - reported (usually) with material when received from vendor

3.2.3.2 Initial Physicochemical Properties of Packing Material (if utilized)

- Bulk chemical composition, mineralogy, porosity, and permeability
  - standard mineralogic and chemical techniques and hydrologic determinations

3.2.3.3 Initial Physicochemical Properties of Backfill

- Bulk Chemical Composition, mineralogy, porosity, and permeability
  - standard mineralogic and chemical techniques and hydrologic determinations

3.2.3.4 Initial Physicochemical Properties of Seals

- Bulk Chemical Composition, types and compositions of solid phases, porosity, and permeability

  - standard mineralogic and chemical techniques and hydrologic determinations

3.2.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

(TO BE COMPLETED BY SEPTEMBER 30)

3.3 WHAT ARE THE CHANGES IN THE GEOCHEMICAL CONDITIONS AND PROCESSES IN THE DISTURBED ZONE THAT MAY OCCUR OVER TIME AS THE RESULT OF REPOSITORY CONSTRUCTION, OPERATION, AND CLOSURE, AND HOW MAY THESE CHANGES AFFECT THE ANTICIPATED REPOSITORY PERFORMANCE?

Issue 3.3 addresses the changes in the geochemical conditions and processes of the disturbed zone that may occur over time, and relates these changes to the prediction of repository performance. ("Disturbed zone means that portion of the controlled area, excluding shafts, whose physical or chemical properties are predicted to change as a result of underground facility construction or heat generated by the emplaced radioactive waste such that the resultant change of properties could have significant effect on the performance of the geologic repository" [10 CFR Part 60.2; 10 CFR Part 960.2].) Ambient geochemical conditions and processes will be affected by numerous actions taken during characterization, selection, operation, and closure of the repository. For example, mining operations will introduce large volumes of air, and may alter groundwater flow patterns and affect mineral assemblages along release pathways. Also, the decay heat from the waste will alter the temperature profile of the setting after emplacement of waste and site closure. Such changes in geochemical conditions and processes could have significant effects on the anticipated repository performance and compliance with regulatory standards. Therefore, knowledge of these changes and their effects on the anticipated repository performance are important aspects of the modeling activity to demonstrate reasonable assurance or reasonable expectation of achieving the necessary degree of waste isolation.

3.3.1 Regulatory Rationale

3.3.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR Part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

Implementation Guidelines - One siting provision (Part 960.3-1) of the implementation guidelines addresses prediction of the affects of waste emplacement on the capability of the host rock to accommodate waste. Information on the thermal, mechanical, chemical, and radiation stresses induced by repository construction, operation, and closure is called for in Appendix IV, Section 960.4-2-3, Rock Characteristics.

Preclosure Guidelines - Preclosure guidelines are detailed in Part 960.5. These guidelines specify the factors to be evaluated in comparing sites on the basis of expected repository performance before closure. No geochemistry guidelines are specified and little geochemical information may be needed to satisfy these preclosure guidelines. Most of the technical preclosure guidelines are related to mechanical aspects of the site rocks and hydrologic characteristics of the site.

Postclosure Guidelines - The postclosure guidelines are listed in Part 960.4. These guidelines are to be considered in evaluating and comparing sites on the basis of expected repository performance after closure. ("Closure means final backfilling of the remaining open operation areas of the underground facility and boreholes after termination of waste emplacement, culminating in the sealing of shafts" [Part 960.2].) Both system and technical guideline qualifying conditions are listed. A "qualifying condition" is defined as a condition that must be satisfied for a site to be considered acceptable with respect to a specific guideline. The system qualifying condition [Part 960.4-1] states that the geologic setting at the site shall allow for physical separation of the radioactive waste from the accessible environment after closure in accordance with the requirements of 40 CFR Part 191, as implemented by the provisions of 10 CFR Part 60. Geochemistry postclosure technical guidelines are detailed in Part 960.4-2-2. The geochemical technical qualifying condition [Part 960.4-2-2(a)] states that the present and expected geochemical characteristics of a site shall be compatible with waste containment and isolation, considering the likely interactions among the radionuclides, host rock, and groundwater, and the characteristics and processes operating within the geologic setting shall permit compliance with the system postclosure guideline qualifying condition [Part 960.4-1].

The postclosure guidelines list favorable geochemistry conditions in Part 960.4-2-2(b). A "favorable condition" is defined as a condition that, though not necessary to qualify a site, is presumed, if present, to enhance confidence that the qualifying condition can be met. The favorable geochemistry conditions are:

Part 960.4-2-2(b)(1) - "The rates and natures of the geochemical processes operating within the geologic setting during the Quaternary Period would, if continued into the future, not affect or would favorable affect the ability of the repository to isolate waste during the next 100,000 years."

Part 960.4-2-2(b)(2) - "Geochemical conditions that promote the precipitation, diffusion into the rock matrix, or sorption of radionuclides; inhibit the formation of particulates, colloids, inorganic complexes, or organic complexes that increase the mobility of radionuclides; or inhibit the transport of radionuclides by particulates, colloids, or complexes."

Part 960.4-2-2(b)(3) - "Mineral assemblages that, when subjected to expected repository conditions, would remain unaltered or would alter to mineral assemblages with equal or increases capability to retard radionuclide transport."

Part 960.4-2-2(b)(4) - "A combination of expected geochemical conditions and a volumetric flow rate of water in the host rock that would allow less than 0.001 percent per year of the total radionuclide inventory in the repository at 1000 years to be dissolved."

Part 960.4-2-2(b)(5) - "Any combination of geochemical and physical retardation processes that would decrease the predicted peak cumulative releases of radionuclides to the accessible environment by a factor of 10 as compared to those predicted on the basis of groundwater travel time without such retardation."

The postclosure guidelines list potentially adverse geochemistry conditions in Part 960.4-2-2(c). A "potentially adverse condition" is defined as a condition that is presumed to detract from expected system performance, but further evaluation, additional data, or mitigating factors may indicate that its effect on the system performance is acceptable. The potentially adverse conditions are:

Part 960.4-2-2(c)(1) - "Groundwater conditions in the host rock that could affect the solubility or the chemical reactivity of the engineered barrier system to the extent that the expected repository performance could be compromised."

Part 960.4-2-2(c)(2) - "Geochemical processes or conditions that could reduce the sorption of radionuclides or degrade rock strength."

Part 960.4-2-2(c)(3) - "Pre-waste-emplacement groundwater conditions in the host rock that are chemically oxidizing."

Other geochemical information is called for in a postclosure guideline for a potentially adverse condition that deals with thermal aspects of rock characteristics. Part 960.4-2-3(c)(2) addresses the potential for such phenomena as the hydration or dehydration of mineral components, brine migration, or other physical, chemical, or radiation-related phenomena that could be expected to affect waste containment or isolation.

No disqualifying condition is identified under the postclosure guidelines for geochemistry [Part 960.4-2-2]. A "disqualifying condition" is defined as a condition that, if present at a site, would eliminate that site from further consideration.

3.3.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

The NRC rules do not directly address the changes which may occur as a result of construction, operation, and closure of a repository. Instead of considering the changes themselves, the rules are primarily performance oriented and, as such, the affect of changes are addressed in issue 3.5. Analysis of the expected performance will require knowledge of some chemical data and information. Rules which establish criteria for the waste package and its components given in Part 60.135 will specifically require knowledge of changes in ambient conditions and processes. A number of geochemistry and geochemistry-related factors are to be considered in the design of the waste packages. These include: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, radiolysis, radiation damage, radionuclide retardation, leaching, thermal loads, and synergistic interactions [Part 60.135(a)(2)].

3.3.1.3 EPA Standards. The EPA has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.3.2 Data and Information Needed to Analyze the Issue

3.3.2.1 Preclosure Period.

Effects of Repository Construction and Operation on Subsurface Temperature. Air ventilated through the shafts and drifts of the Hanford Site repository will lower wall rock temperatures and humidity and perhaps also decrease the temperatures of the rocks immediately above the repository horizon. The long-term effects of this thermal disturbance, if any, should be assessed.

Effects of Repository Construction and Operation on Hydrogeochemical Processes and Parameters

- Changes in the patterns and rates of groundwater flow

It will be important to determine how the patterns and rates of groundwater flow have been altered by repository siting and construction activities (exploratory drilling, shaft and drift construction, etc.) This information will be required for modeling changes in subsurface groundwater flow that will begin to occur immediately after repository closure.

- Changes in the porosities and permeabilities of rocks near man-made openings

It is possible that construction and operation of the repository will have significant effects on the rocks in the structurally disturbed zone around the engineered facility. In particular, it is likely that the porosities and permeabilities of these rocks will be altered by the drilling and blasting that will be required to construct this facility. Therefore, it would be informative to obtain information on the porosities and permeabilities of the rocks in the structurally disturbed zone of the Hanford Site repository.

Effects of Repository Construction and Operation on Groundwater and Rock-Groundwater Interactions

- Changes in the physicochemical properties of groundwater

It will be important to determine how repository construction and operation activities affect key physicochemical properties of groundwaters (the major and minor element chemistry of solute material, amounts and composition of dissolved gases, the quantity and characteristics of organic matter, speciation, pH, redox conditions, and the quantities and compositions of suspended colloids and particulates). This is particularly true for groundwaters that flow through the structurally disturbed rocks immediately adjacent to the engineered facility.

- Changes in rock-groundwater interactions along groundwater flow paths

It should be determined whether repository construction and operation activities result in any significant changes in rock-groundwater interactions along groundwater flow paths. This information will be required for modeling rock-groundwater interactions along groundwater flow paths during the postclosure period.

Effects of Repository Construction and Operation on Mineralogy

- Mineral assemblages and the chemical compositions of minerals

It should be determined whether repository construction and operation activities have any significant effects on the minerals and mesostasis in the rocks in the structurally disturbed zone of the Hanford Site repository.

3.3.2.2 Postclosure Period.

Changes in Subsurface Temperature During the Postclosure Period.

- Evolution of the thermally disturbed zone in the site system

Satisfactory repository performance-assessment modeling will require detailed information on the expansion and contraction of the thermally disturbed zone that will develop in the Hanford Site system during the postclosure period.

Changes in Hydrogeochemical Processes and Parameters During the Postclosure Period -

- Changes in the patterns and rates of groundwater flow

Development of a disturbed zone in the Hanford Site repository site is apt to have major effects on the patterns and rates of groundwater flow in the rocks adjacent to the engineered facility. Therefore, a satisfactory postclosure hydrologic model of groundwater flow in the disturbed zone of the Hanford Site repository is required for defensible predictions of the performances of engineered barrier materials and site rocks.

- Changes in the porosities and permeabilities of rocks

During the postclosure period, it is possible that hydrothermal alteration will have significant effects on the porosities and permeabilities of the rocks adjacent to the engineered facility. This might occur, for example, if circulating groundwaters transport significant quantities of silica away from the comparatively hot rocks near waste packages toward cooler rocks above the repository horizon. This is of particular concern in a mesostasis-rich zone. Therefore, some consideration should be given to the effects of hydrothermal alteration on the hydrologic properties of the rocks adjacent to the engineered facility.

Changes in the Physicochemical Properties of Groundwater and Rock-Groundwater Interactions -

- Changes in the physicochemical properties of groundwater during the postclosure period

Development of a disturbed zone in the Hanford Site repository site is apt to have major effects on the physicochemical properties of groundwaters that flow through the engineered facility and nearby rocks. In addition to increased rates of rock-groundwater interactions and attendant changes in groundwater composition caused by rising temperatures, it is possible that gamma radiation emanating from waste canisters will induce radiolytic reactions in the groundwaters that flow near waste packages. The latter possibility should be investigated because canister performance and radionuclide containment could be compromised if radiolytic reactions elevate the redox states of groundwaters in the very near field.

- Kinetics of rock-groundwater interactions

Increases in the temperatures of the rocks in the thermally disturbed zone of the Hanford Site repository site are likely to be accompanied by increased rates of rock-groundwater interactions. This is particularly true in a mesostasis-rich zone. Therefore, it is important to determine how elevated temperatures will affect the kinetics of geochemical interactions between basalt, crystalline, and glassy rocks and coexisting groundwaters.

Changes in Mineralogy During the Postclosure Period -

- Thermodynamic stabilities and reaction kinetics of the minerals in the thermally disturbed zone of the Hanford Site repository

Development of a disturbed zone in the Hanford Site system will result in increases in temperature and changes in groundwater composition in the rocks adjacent to the engineered facility. Therefore, it should be determined how elevated temperatures and changes in groundwater composition will affect the thermodynamic stabilities and reaction kinetics of the minerals and mesostasis in the thermally disturbed zone of the Hanford Site repository.

- Chemical compositions of the minerals in the thermally disturbed zone of the Hanford Site repository

It should be determined whether hydrothermal alteration will have any significant effects on the chemical compositions of the minerals and mesostasis in the thermally disturbed zone of the Hanford Site repository.

- Solubilities of the minerals in the thermally disturbed zone of the Hanford Site repository

Development of a disturbed zone in the Hanford Site system will result in increases in temperature and changes in groundwater composition in the rocks adjacent to the engineered facility. Therefore, it should be determined how elevated temperatures and changes in groundwater composition affect the solubilities of the minerals and mesostasis in Hanford Site rocks.

- Radionuclide-sorption characteristics of the minerals in the thermally disturbed zone of the Hanford Site repository

It should be determined whether low-temperature hydrothermal alteration will have any significant effects on the radionuclide-sorption characteristics of the phases in the thermally disturbed zone of the Hanford Site repository. Also, it should be determined whether or not low-temperature hydrothermal alteration changes the kinds and quantities of radionuclide-sorbing minerals in this zone.

Changes in Petrology During the Postclosure Period -

- Changes in the bulk chemical compositions of rocks in the site system

It should be determined whether rock-groundwater interactions in the thermally disturbed zone of the repository will lead to any significant changes in the bulk chemical compositions of the rocks in this zone.

3.3.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.3.3.1 Preclosure Period

Effects of Repository Construction and Operation on Subsurface Temperature

- standard thermal models

Effects of Repository Construction and Operation on Hydrogeochemical Processes and Parameters

- Changes in patterns and rates of groundwater flow
  - hydrology subject (likely to be one- and two-phase models supported by laboratory and field tests)
- Changes in the porosities and permeabilities of rocks near man-made openings
  - hydrology subject (models supported by laboratory and in situ tests likely approach)

Effects of Repository Construction and Operation on Groundwater and Rock-Groundwater Interactions

- Changes in physicochemical properties of groundwater
  - rock/water tests and in situ testing will be necessary to delineate potential changes; may be complemented by application of geochemical models
- Changes in rock/groundwater interactions along groundwater flow paths
  - see item immediately above

Effects of Repository Construction and Operation on Mineralogy

- Mineral assemblages and the chemical compositions of minerals
  - laboratory studies will be necessary to determine potential effects; in situ tests may be beneficial

3.3.3.2 Postclosure Period

Changes in Subsurface Temperature During Postclosure Period

- Evolution of the thermally disturbed zone in the site system
  - standard thermal models should be used

Changes in Hydrogeochemical Processes and Parameters During the Postclosure Period

- Changes in the patterns and rates of groundwater flow
  - hydrology subject
- Changes in the porosities and permeabilities of rocks
  - hydrology subject (likely to be models supported by laboratory and field tests)

Changes in the Physicochemical Properties of Groundwater and Rock-Groundwater Interactions

- Changes in the physicochemical properties of groundwater during the postclosure period
- Kinetics of rock-groundwater interactions
  - perform rock/water tests at appropriate temperature and pressure conditions to elucidate potential changes in the groundwater and solid phases present in the rocks; the atmosphere in these tests should be controlled so as to represent that present in the host-rock environment; some tests in the presence of radiation may be necessary
  - tests should be complemented by geochemical modeling to the extent practicable

Changes in Mineralogy During the Postclosure Period

- Thermodynamic stabilities and reaction kinetics of the minerals in the thermally disturbed zone of the Hanford Site repository
- Chemical compositions of the minerals in the thermally disturbed zone of the Hanford Site repository

- Solubilities of the minerals in the thermally disturbed zone of the Hanford Site repository
    - perform rock/water tests at appropriate temperature and pressure conditions to elucidate potential changes in the groundwater and solid phases present in the rocks; the atmosphere in these tests should be controlled so as to represent that present in the host-rock environment; some tests in the presence of radiation may be necessary
    - tests should be complemented by geochemical modeling to the extent practicable
- Radionuclide-sorption characteristics of the minerals in the thermally disturbed zone of the Hanford Site repository
    - perform sorption tests on materials from the rock/water interactions tests (see section 3.6.3 for details on sorption data and methods)

Changes in Petrology During the Postclosure Period

- Changes in the bulk chemical compositions of rocks in the site system
    - perform rock/water tests at appropriate temperature and pressure conditions to elucidate potential changes in the groundwater and solid phases present in the rocks; the atmosphere in these tests should be controlled so as to represent that present in the host-rock environment; some tests in the presence of radiation may be necessary
    - tests should be complemented by geochemical modeling to the extent practicable

3.3.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

(TO BE COMPLETED BY SEPTEMBER 30)

3.4 HOW WILL THE CHANGES IN THE GEOCHEMICAL CONDITIONS AND PROCESSES THAT MAY OCCUR OVER TIME AS A RESULT OF REPOSITORY CONSTRUCTION, OPERATION, AND CLOSURE AFFECT THE ANTICIPATED PERFORMANCE OF THE ENGINEERING MATERIALS (PACKING, BACKFILL, AND SEALS) UTILIZED IN THE REPOSITORY?

Issue 3.4 addresses the effects that changes in geochemical conditions and processes may have upon the anticipated performance of engineering materials placed in the repository during operation and closure. It is expected that engineering materials may be utilized to close man-made openings such as boreholes, tunnels, shafts, drifts, etc. which have been made in the geologic setting as a result of various site characterization, or repository construction and operation actions. Packing may be used in the annular space around the waste canister, backfill may be used to close tunnels and shafts, and seals may be used to prevent groundwater flow through boreholes, tunnels, shafts, etc. The anticipated performance of these materials may be dependent upon specific geochemical conditions or processes, and analysis of how changes in these conditions and processes affect the performance of these engineering materials is an important aspect of the predictive modeling of waste isolation by the repository.

3.4.1 Regulatory Rationale

3.4.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

The DOE guidelines do not specifically mention engineering materials, such as packing, backfill, and seals, that may be used in the construction, operation, and closure of a repository. The guidelines are designed for application in the site selection process, and the guidelines specifically state that the possible isolation due to the use of engineered barriers is not to be relied upon to compensate for deficiencies in the geologic media [Part 960.3-1-5].

3.4.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

Rules applicable to the seals for shafts and boreholes are given in Part 60.134. The general criterion states that seals shall be designed so that shafts and boreholes do not become pathways that compromise the ability of the geologic repository to meet the performance objectives of the period following permanent closure [Part 60.134(a)]. Also, the materials and placement of seals shall be selected so as to reduce radionuclide migration through existing pathways [Part 60.134(b)(2)].

3.4.1.3 EPA Standards. The EPA has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.4.2 Data and Information Needed to Analyze the Issue

3.4.2.1 Canister Metal.

Preclosure Period -

- Effects of prolonged exposure to decay heat, gamma radiation, and air

Information is needed on whether the integrity of canister metal will be affected significantly by prolonged heating, gamma irradiation, and exposure to air.

Postclosure Period -

- Effects of prolonged exposure to decay heat, gamma radiation, and groundwater

Soon after repository closure, the waste canisters in the Hanford Site repository will come into direct contact with groundwater at elevated temperatures. The groundwater and gamma radiation are expected to compromise waste containment by promoting canister corrosion. Therefore, information is needed on how the performance of canister metal is influenced by the geochemical conditions that develop near waste canisters during the postclosure period.

3.4.2.2 Initial Physicochemical Properties of Packing Material (if Utilized

The most recent reference design for waste packages in the proposed Hanford Site repository (reference) does not include packing material. However, it is possible that future designs may include this material. Therefore, data and information needs concerning the physicochemical characteristics of packing material are discussed briefly below.

Preclosure Period -

- Initial porosity and permeability. Effects of decay heat, gamma radiation, and short-term exposure to air

Satisfactory prediction of the performance of packing material is contingent upon obtaining information on how this material is affected by decay heat, gamma radiation, and exposure to air during the preclosure period.

Postclosure Period -

- Effects of prolonged exposure to decay heat, gamma radiation, and groundwater

Modeling of the long-term (postclosure) performance of packing material requires data on the effects of exposure to decay heat, gamma radiation, and groundwater. Hydrothermal alteration of the solid phases in the packing material could compromise the performance of packing material by changing the porosity and permeability of packing material.

3.4.2.3 Backfill.

Preclosure Period -

- Effects of short-term exposure to air

It should be determined whether exposure to air during the preclosure period will have any significant effects on the long-term (postclosure) performance of backfill.

Postclosure Period -

- Effects of prolonged exposure to throughflowing groundwater

It should be determined whether groundwater-backfill interactions during the postclosure period will have any significant effects on the compositions of throughflowing groundwaters and the quantities of colloids and particulates suspended in these groundwaters.

3.4.2.4 Seals.

Preclosure Period -

- Effects of exposure to air

Seals will be exposed to air for indefinite periods of time prior to emplacement in the repository. Therefore, it should be determined whether pre-emplacement exposure to air will have any significant effects on the long-term (postclosure) performance of repository seals.

Postclosure Period -

- Effects of prolonged exposure to throughflowing groundwater

Satisfactory prediction of the performance of seals during the postclosure period requires information on how sealing material is affected by long-term exposure to throughflowing groundwater.

3.4.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.4.3.1 Canister Metal

Preclosure Period

- Effects of prolonged exposure to decay heat, gamma radiation, and air
    - corrosion subject

Postclosure Period

- Effects of prolonged exposure to decay heat, gamma radiation, and groundwater
    - corrosion subject, but the conditions of testing should be defined by tests discussed in section 3.3.3

3.4.3.2 Packing Material (if present)

Preclosure Period

- Initial porosity and permeability. Effects of decay heat, gamma radiation, and short-term exposure to air
    - laboratory tests should be used to alter the material and then standard methods for porosity and permeability should be applied.

Postclosure Period

- Effects of prolonged exposure to decay heat, gamma radiation, and groundwater
    - laboratory tests under appropriate geochemical conditions should be used to alter the material and then the porosity and permeability determined via standard methods

3.4.3.3 Backfill

Preclosure Period

- Effects of short-term exposure to air
    - laboratory tests using relevant geochemical conditions should be performed; any changes in the properties of the backfill material should be assessed using standard mineralogical and chemical techniques; changes in porosity and permeability should also be determined

Postclosure Period

- Effects of prolonged exposure to throughflowing groundwater
    - see preclosure discussion

3.4.3.4 Seals

Preclosure Period

- Effects of short-term exposure to air
    - see 3.4.3.3

Postclosure Period

- Effects of prolonged exposure to throughflowing groundwater
    - see 3.4.3.3

3.4.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

(TO BE COMPLETED BY SEPTEMBER 30)

3.5 WHAT ARE THE GEOCHEMICAL CONDITIONS AND PROCESSES THAT MAY AFFECT THE RADIONUCLIDE SOURCE TERM AT THE BOUNDARIES OF (1) THE WASTE PACKAGES DURING THE CONTAINMENT PERIOD AND (2) FROM THE ENGINEERED BARRIER SYSTEM IN THE POSTCONTAINMENT PERIOD, AND HOW MAY THE ANTICIPATED REPOSITORY PERFORMANCE BE INFLUENCED?

The geochemical conditions and processes that may affect the radionuclide source term or release rate are analyzed in issue 3.5. The time after repository closure is divided into two periods that have different performance objectives. During the containment period of not less than 300 years or more than 1000 years, NRC rules require that containment of waste by the waste package must be substantially complete. In the post-containment period after 300 to 1000 years, the allowable release rate of radionuclides from the engineered barrier system is specified by NRC rules. Mathematical modeling will be utilized to predict the source term or release rate of radionuclides during these post-closure periods, and geochemical data and information will be important input required by the modeling activity. An understanding of the relevant geochemical conditions and processes, and their influence on the source term, may be crucial to demonstrating reasonable assurance of anticipated repository compliance with the relevant regulations.

3.5.1 Regulatory Rationale

3.5.1.1 DOE Guidelines

The DOE has issued regulatory guidelines [10 CFR part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

The postclosure system guideline qualifying condition [Part 960.4-1(a)] states that the geologic setting at the site shall allow for the physical separation of radioactive waste from the accessible environment after closure in accordance with the requirements of 40 CFR Part 191, Subpart B, as implemented by the provisions of 10 CFR 60. As discussed below (Section 3.5.1.2), provisions of 10 CFR 60 deal with the permissible radionuclide release rate, or source term, in the postclosure period. Geochemical data will be needed to support modeling of the source term. Other than that qualifying condition, the source term at the waste package is not specifically addressed in the DOE guidelines.

3.5.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10], although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

Performance Objectives - The performance objectives first set general objectives for the performance of the repository operations area through closure [Part 60.111(a)], for the option of retrievability of waste at up to 50 years after the start of waste emplacement [Part 60.111(b)], and for the overall performance of the repository after closure to assure that radioactive material releases shall conform to the EPA standards [Part 60.112].

The general provisions for the performance of particular barriers after closure differentiate between performance during the period when radiation and thermal conditions are dominated by decay, i.e., the period of containment, and for small fractional releases over long times, i.e., the post-containment period [Part 60.113(a)]. A subpart of the general provision specifically addresses the need for analysis of groundwater information for disposal in the saturated zone [Part 60.113(a)(i)(B)].

The performance of particular barriers after closure are detailed in Part 60.113. The rules specified in Part 60.113 are important to the analysis of geochemical issues because they establish the repository performance that must result from the action of particular barriers at specified times after closure. The containment of waste within the waste package must be substantially complete for the period of containment [Part 60.113(a)(1)(i)(A)]. ("Waste package is defined to mean the waste form and any containers, shielding, packing and other absorbent materials immediately surrounding an individual waste container" [Part 60.2].) "Substantially complete" is not described in the definitions [Part 60.2]. The period of containment is required to be not less than 300 years nor more than 1000 years following permanent closure [Part 60.113(a)(1)(ii)(A)]. ("Permanent closure means final backfilling of the underground facility and the sealing of shafts and boreholes" [Part 60.2].) Computer modeling will be necessary to predict conformance with these rules, and geochemical data and information will be important input to the modeling activity.

Following the containment period, the release rate of any radionuclide from the engineered barrier system shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure of the repository [Part 60.113a)(1)(ii)(B)]. ("Engineered barrier system is defined to mean the waste packages and the underground facility" [Part 60.2].) It is important to note that as a result of this wording, the rule specifies release rates after the containment period from the overall engineered facility, and not from the individual waste packages as in the containment period. An exception to the one in 100,000 release rate rule is provided for any radionuclide which is released at a rate less than 0.1% of the calculated total release rate. The calculated total release rate shall be taken to be one part in 100,000 per year of the inventory of radioactive waste that remains after 1000 years of decay after original emplacement [Part 60.113(a)(1)(ii)(B)]. Note that 1000 years after original emplacement may be a slightly shorter time than 1000 years after permanent closure. Computer modeling will be necessary to predict conformance with these rules, and geochemical data and information will be important input to the modeling activity.

Part 60.113 also contains a clause that allows the NRC to approve or specify some other release rate, containment period, etc., on a case-by-case basis [Part 60.113(b)]. Various types of information are to be taken into account in such a performance variance, including the geochemical characteristics of the host rock, surrounding strata, and groundwater [Part 60.113(b)(3)].

Design Criteria for the Waste Package - Rules which establish criteria for the waste package and its components are given in Part 60.135. A number of geochemistry and geochemistry-related factors are to be considered in the design of the waste packages. These include: solubility, oxidation/reduction reactions, corrosion, hydriding, gas generation, thermal effects, radiolysis, radiation damage, radionuclide retardation, leaching, thermal loads, and synergistic interactions [Part 60.135(a)(2)].

3.5.1.3 EPA Standards. The NRC has promulgated regulatory standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository. Therefore, EPA standards are analyzed only under Issue 3.6.

3.5.2 Data and Information Needed to Analyze the Issue

3.5.2.1 Containment Period. Information on the geochemical processes and conditions that affect corrosion and radionuclide release (post-containment) is essential to performance assessments of engineered barrier systems. The nature of these processes and conditions is needed as a function of time (through 1000 years for the containment period) so that corrosion and source term models can account for changing conditions and processes. Ranges and distributions are required for geochemical conditions essential to the performance of the engineered barrier system. The nature, extent, and probability of occurrence is needed for the key processes. This probabilistic information is needed to support performance assessment calculations addressing the reliability of the engineered barrier system. The processes and conditions that may be active in and around the engineered barrier system are discussed below.

Temperature: Effects corrosion processes, geochemical conditions, and radionuclide release from engineered barrier system. Information is needed as a function of time and distance within the engineered barrier system.

Pressure: Fundamental parameter that is most important to the failure of the waste package canister. Impacts other processes and conditions, but not as importantly as temperature. Information is needed on both lithostatic and hydrostatic pressures as a function of time and distance within the engineered barrier system.

Groundwater Chemistry: Effects corrosion processes, geochemical conditions, and radionuclide release from engineered barrier system.

- redox, pH, major and minor element chemistry
- organics, colloids, particulates
- should consider effects of temperature, pressure, gamma-radiation, and rock/water/barrier interactions for all of the above

Solids: Natural and engineered materials, as well as the presence of their alteration products will impact the overall performance of the engineered barrier system. It will be important to quantify the corrosion of metallic canisters, the alteration of packing material (changing hydrologic-isolation performance and sorption characteristics), the thermal effects on the physical nature of the waste form, etc. The nature of these solids at the time of failure and beyond is needed so that release models can account for any processes that promote or inhibit the release and transport of radionuclides.

- waste form, canister material, packing, crushed rock, and host rock
- should consider effects from temperature, pressure, gamma-radiation, and rock/water/barrier interactions
- information should include: (1) bulk composition, (2) mineralogy, surface characterization, and nature of failure for barriers (i.e, type and extent of canister corrosion)

Hydrologic Setting: Information is needed on the flow field around the engineered barrier system prior to the time of failure and beyond so that geochemical conditions that affect corrosion and radionuclide release can be quantified.

- porosity and permeability for each barrier (component) that may affect the flow field (e.g., host rock, packing, canister, waste form). General information on the ambient and post-closure flow-field will also be required.

3.5.2.2 Post-Containment Period. Information on the geochemical processes and conditions that affect radionuclide release is essential to performance assessments of engineered barrier systems. The nature of these processes and conditions is needed as a function of time (from time of failure through 10,000 years) so that source term models can account for changing conditions and processes. The source term models will be used to evaluate compliance with the slow-release criterion and to provide a source term for transport models addressing the 10,000 year cumulative release criterion. Ranges and distributions are required for geochemical conditions essential to the performance of the engineered barrier system. The nature, extent, and probability of occurrence is needed for the key processes. This probabilistic information is needed to support performance assessment calculations addressing the reliability of the engineered barrier system. The processes and conditions that may be active in and around the engineered barrier system are discussed below.

Temperature: Effects geochemical conditions that control the release of radionuclides from the engineered barrier system. Information is needed as a function of time and distance within the engineered barrier system.

Pressure: Fundamental parameter that is most important to the failure of the waste package canister. Impacts other processes and conditions, but not as importantly as temperature. Information is needed on both lithostatic and hydrostatic pressures as a function of time and distance within the engineered barrier system.

Groundwater Chemistry: Effects geochemical conditions thus radionuclide release from engineered barrier system.

- redox, pH, major and minor element chemistry
- organics, colloids, particulates
- should consider effects of temperature, pressure, gamma-radiation, alpha-radiation, and rock/water/barrier interactions for all of the above

Solids: Natural and engineered materials, as well as the presence of their alteration products will impact the overall performance of the engineered barrier system. It will be important to quantify the corrosion of metallic canisters, the alteration of packing material (changing hydrologic-isolation performance and sorption characteristics), the thermal effects on the physical nature of the waste form, etc. The nature of these solids at the time of failure and beyond is needed so that release models can account for any processes that promote or inhibit the release and transport of radionuclides.

- waste form, canister material, packing, crushed rock, and host rock
- should consider effects from temperature, pressure, gamma-radiation, and rock/water/barrier interactions
- information should include: (1) bulk composition, (2) mineralogy, surface characterization, and nature of failure for barriers (i.e, type and extent of canister corrosion)

Hydrologic Setting: Information is needed on the flow field around the engineered barrier system prior to the time of failure and beyond so that geochemical conditions that affect corrosion and radionuclide release can be quantified.

- porosity and permeability for each barrier (component) that may affect the flow field (e.g., host rock, packing, canister, waste form). General information on the ambient and post-closure flow-field will also be required.

Source-Term Parameters: The following parameters are typically used in source models. The parameters can be used to provide a concentration and rate of mass transfer at various points away from the waste packages. The information can be used to homogenize release across the entire repository also. Information on reactions within the engineered barrier system is important because these reactions can slow down or speed up release of radionuclides from the waste form. Information on the speciation of radionuclide-bearing solutions is not essential to source models, but is essential for performing acceptable sorption tests so that far-field transport models will be reliable.

- aqueous concentration of all key radionuclides at waste form interface (e.g., "solubility," steady-state concentration, dissolution rates)
- diffusion coefficients for all key radionuclides in solutions of interest
- "retardation" reactions that may occur within the engineered barrier system (e.g., ion-exchange, ppt, redox, etc.)

- speciation of solutions likely to be released from the engineered barrier system
- should consider effects of kinetics, groundwater flow rate, temperature, pressure, radiation (alpha and gamma), and rock/water/barrier interactions

3.5.3 Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information

3.5.3.1 Containment Period

- Temperature
  - standard thermal models should be adequate to predict temperatures around the waste package
- Pressure
  - see 3.1.3.2 for determination of hydrostatic and lithostatic pressure
  - thermomechanical models will be needed to predict the stress fields around the waste package for analysis of canister failure
- Groundwater Chemistry
  - see 3.3.3 and 3.3.4
- Solids
  - see 3.3.3 and 3.3.4
- Hydrologic Setting
  - hydrology subject

3.5.3.2 Post-Containment Period

- Temperature, Pressure, Groundwater Chemistry, Solids, Hydrologic Setting

    - see 3.5.3.1

- Source Term Parameters

    - concentrations of radionuclides:

        Waste/barrier/water/rock interactions tests will be required to establish concentrations for all the important radionuclides. The tests should be conducted using relevant geochemical conditions and materials. Standard methods for solution and solid analyses should be employed. Criteria to establish that "steady state" has been reached should be developed. To the extent practicable, an understanding of the reactions involved should be established so that extrapolations of the data can be accomplished with geochemical models.

        Parameters to be considered in the design of the experiments include: time, groundwater flow rate, temperature, pressure, and radiation.

    - diffusion coefficents:

        Diffusion coefficients should be determined using standard methods for multicomponent systems. Conditions of chemistry, temperature, etc. should be based upon results of tests and modeling as outlined in sections 3.3.3 and 3.4.3

    - retardation reactions within engineered system:

        Sorption tests should be completed using relevant geochemical conditions (see 3.6.3 for details of sorption procedures).

    - speciation of solutions:

        To the extent practicable, the speciation of radionuclides in the resulting solutions should be determined. This determination could be acommplished using standard speciation techniques or geochemical models. As an alternative, the solutions from these tests could be directly used in sorption tests designed to assess the far-field transport of radionuclides.

3.5.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

(TO BE COMPLETED BY SEPTEMBER 30)

3.6 WHAT GEOCHEMICAL CONDITIONS AND PROCESSES AFFECT THE TRANSPORT OF MOBILIZED RADIONUCLIDES THROUGH THE GEOLOGIC SETTING AND THE RELEASE OF RADIONUCLIDES TO THE ACCESSIBLE ENVIRONMENT, AND HOW MAY THE ANTICIPATED REPOSITORY PERFORMANCE BE INFLUENCED?

Issue 3.6 analyzes the geochemical conditions and processes that affect the transport of mobilized radionuclides through the geologic setting to the accessible environment. Issue 3.5 analyzed the source term or release rate of radionuclides from the waste packages or the engineered facility which results in mobilized radionuclides. The NRC rules analyzed in issue 3.5 differentiate between two time periods after disposal; the period of substantially complete containment of radionuclides by the individual waste packages (not less than 300 years or more than 1000 years), and the post-containment period where the allowable radionuclide release rate from the engineered facility is one part in 10,000 of the 1000 year inventory of each radionuclides. The EPA standards analyzed in this issue do not address those arbitrary time periods in the NRC rules, but instead deal with releases to the accessible environment for times up to 10,000 years after disposal.

The rate of movement or retardation of mobilized radionuclides in groundwater are subject to various geochemical conditions and processes during transport through the geologic setting. The EPA standards establish the cumulative release limits for 10,000 years after disposal for various radionuclides to the accessible environment. Mathematical modeling will be employed to demonstrate anticipated compliance with these standards, and geochemical data and information will be important input for the modeling activity.

3.6.1 Regulatory Rationale

3.6.1.1 DOE Guidelines. The DOE has issued regulatory guidelines [10 CFR part 960] for the recommendation of repository sites for the geologic disposal of high-level waste and spent fuel. The guidelines will be used in the site selection process. The guidelines establish performance objectives, define technical requirements, and specify how the site selection process will be implemented. Various implementation guidelines, preclosure guidelines, and postclosure guides explicitly or implicitly require knowledge of geochemical data and information.

The postclosure system guideline qualifying condition [Part 960.4-1(a)] states that the geologic setting at the site shall allow for the physical separation of radioactive waste from the accessible environment after closure in accordance with the requirements of 40 CFR Part 191, Subpart B, as implemented by the provisions of 10 CFR 60. As discussed below (Section 3.5.1.3), provisions of 40 CFR 191 deal with the cumulative release rates of radionuclides to the accessible environment. Geochemical data will be needed to support modeling of these release rates. Other that qualifying condition, the transport and release of radionuclides to the accessible environment is not specifically addressed in the DOE guidelines.

3.6.1.2 NRC Rules. The NRC has prescribed regulatory rules [10 CFR Part 60] which govern the licensing of the DOE to construct a geologic repository [Part 60.3(b)], to receive radioactive material at a repository [Part 60.3(a), and for permanent closure of a repository [Part 60.51]. A license is not required for site characterization activities [Part 60.10],

although a Site Characterization Plan is to be submitted by the DOE [Part 60.16] and reviewed by the NRC [Part 60.18]. The rules specify the contents of a license application [Part 60.21]. The application shall include a Safety Analysis Report which includes a description of the site [Part 60.21(c)(1)(i)] and an assessment of the anticipated performance of the repository [Part 60.21(c)(1)(ii)]. The rules establish technical criteria [Part 60, Subpart C] for, among other things, performance objectives, siting criteria, and design criteria. A number of these technical criteria explicitly or implicitly require knowledge of geochemical data and information.

The NRC rules do not directly address releases of radionuclides to the accessible environment. The overall system performance objective states that the performance of the setting and the engineered barrier systems shall be designed so as to assure that releases of radionuclides to the accessible environment conform to standards established by the EPA [Part 60.122].

3.6.1.3 EPA Standards. The EPA has promulgated standards for the management and disposal of spent nuclear fuel, and high-level and transuranic wastes [40 CFR Part 191]. The focus of these standards is on protection of the public and, thus, the standards address only releases of radioactivity to the environment. The standards do not address the characterization or selection of a repository site, nor do the standards contain requirements for the performance of the geologic barriers or the engineered barriers which may be present in a repository.

The EPA standards are designed to limit the exposure of members of the public from the management and storage of spent fuel, or high-level or transuranic wastes [Part 191, Subpart A], and sets requirements for disposal of these materials [Part 191, Subpart B]. The primary standards for disposal are long-term containment requirements that limit projected releases of radioactivity to the accessible environment for 10,000 years after disposal. ("Accessible environment means: (1) the atmosphere; (2) land surfaces; (3) surface waters; (4) oceans, and (5) all of the lithosphere that is beyond the controlled area" [Part 191.12(k)]. "Controlled area means: (1) a surface location, to be identified by passive institutional controls, that encompasses no more than 100 square kilometers and extends horizontally no more than five kilometers in any direction from the outer boundary of the original location of the radioactive wastes in a disposal system, and (2) the subsurface underlying such a surface location" [Part 191.12(g)].) Assurance requirements are specified to provide confidence that the containment requirements will be met. Finally, a set of groundwater protection requirements are also established for the period of 1000 years after disposal.

Containment Requirements - The containment requirements are detailed in Part 191.13. The standard states that the disposal systems (any combination of engineered and geologic barriers) shall provide a reasonable expectation that the cumulative releases of radionuclides to the accessible environment shall: (1) have a likelihood of less than one chance in 10 of exceeding the quantities calculated according to Table 1, Appendix A, and (2) have a likelihood of less than one chance in 1000 of exceeding 10 times the quantities calculated according to Table 1, Appendix A [Part 191.13(a)]. This standard is the primary containment requirement which details the required performance of a repository for 10,000 years, and, as such, it must be carefully and thoroughly analyzed.

"Reasonable expectation" is not specifically defined, however the concept is dealt with under Part 191.13(b) which states: "Performance assessments need not provide complete assurance that the requirements of 191.13(a) will be met. Because of the long time period involved and the nature of the events and processes of interest, there will inevitably be substantial uncertainties in projecting disposal system performance. Proof of the future performance of a disposal system is not to be had in the ordinary sense of the word in situations that deal with much shorter time frames. Instead, what is required is a reasonable expectation, on the basis of the record before the implementing agency, that compliance with 191/13(a) will be achieved." Guidance for the implementation of the containment requirement is included in Part 191, Appendix B. The guidance states that compliance will involve predicting the likelihood of events and processes that may disturb the disposal system. In making these predictions, the guidance states that it will be appropriate to make use of rather complex computational models, analytical theories, and prevalent expert judgement relative to the numerical predictions. The guidance suggests that numerical predictions may be supplemented with qualitative judgments.

The release limits which apply to the containment requirement are detailed in Part 191, Appendix A, Table 1. Cumulative release limits for

10,000 years after disposal are given for a number of individual radionuclides and groups of radionuclides. ("Disposal means permanent isolation of spent nuclear fuel or radioactive waste from the accessible environment with no intent of recovery, whether or not such isolation permits the recovery of such fuel or waste. For example, disposal of waste in a mined geologic repository occurs when all of the shafts to the repository are backfilled and sealed" [Part 191.02(1)].) Thus, the EPA term "disposal" is equivalent to the NRC term "permanent closure". Table 1 of Appendix A to Part 191 is repeated below. A number of extended footnotes to Table 1 define units of waste and explain the application of the release limits to different types of waste [Part 191, Appendix A]. These footnotes will have to be carefully examined and considered in order to apply the radionuclide release limits in Table 1 to the analysis of the anticipated performance of a given repository.

Considering the relevant standard [Part 191.13] and associated guidance, it seems apparent that resolution of Issue 3.6 may require considerable data and information descriptive of the geochemical conditions and processes which affect radionuclide migration through the geologic setting. As a consequence of the containment requirement of cumulative release limits for individual radionuclides and the associated release limit units for specific types of waste and disposal systems, the performance required of the geologic setting at a specific repository will be dependent on the mixture and types of wastes which are assumed to be emplaced. Thus, analysis of the affect of geochemical or other geotechnical conditions and processes with regard to Issue 3.6 cannot be made independent of the assumed waste content of the repository upon closure. This need for waste data in addition to data and information for the geochemical conditions and processes may appreciably complicate the quantitative analysis of Issue 3.6.

Groundwater Protection Requirements - The groundwater protection requirements [Part 191.16] are designed to insure that, for 1000 years after disposal, any water drawn from a special source shall not exceed the EPA interim drinking water standards as specified in 40 CFR Part 141. (A special source of groundwater includes waters that are within the controlled area, are supplying drinking water for thousands of people, and are irreplaceable in that no alternative drinking water is available to that populace [Part 191.12(o)].) Application of this standard seems to require that, for 1000 years after repository closure, very little to essentially no radioactivity may be released from the waste into groundwaters. This standard may be consistent with an NRC rule requiring a containment period of substantially complete containment of waste by the waste package for 1000 years after closure, but seems potentially inconsistent with a shorter period of time for the NRC containment period, for example such as 300 years.

3.6.2 Data and Information Needed to Analyze the Issue

The data and information needed to analyze Issue 3.6 is primarily associated with the EPA 10,000-year-cumulative-radionuclide-containment-requirement standard [40 CFR Part 191.13(a)]. In this evaluation, the radionuclides are assumed to be transported by flowing groundwater, either

Table 1. Release limits for containment requirments[a]

(Cumulative releases to the accessible environment for 10,000 years after disposal)

Radionuclide	Release limit per 1000 MTHM[b] or other unit of waste (see notes) (Ci)
Americium-241 or -243	100
Carbon-14	100
Cesium-135 or -137	1000
Iodine-129	100
Neptunium-237	100
Plutonium-238, -239, -240, or -242	100
Radium-226	100
Strontium-90	1000
Technetium-99	10000
Thorium-230 or -232	10
Tin-126	1000
Uranium-233, -234, -235, -236, or -238	100
Any other alpha-emitting radionuclide with a half-life greater than 20 years	100
Any other radionuclide with a half-life greater than 20 years that does not emit alpha particles	1000

[a]Table is from 40 CFR 191, Appendix A

[b]MTHM = metric ton of heavy metal, i.e., uranium, plutonium, etc.

as solutes, colloids, or particulates. Geochemical processes are important in controlling the mobility of radionuclides in the geologic setting and the rate of release of radionuclides to the accessible environment, and important processes are discussed in the following section. The action of these processes in the various hydrogeologic regimes at the Hanford Site are then considered in a subsequent section. The mathematical modeling methodology used to predict the cumulative radionuclide release rates is yet to be established. In this situation, it may not be possible to anticipate all the data and information needed to predict the effects of radionuclide dissolution and precipitation processes in the modeling activity. Interaction between the modelers and the geochemists should be an ongoing activity to insure that requisite data and information becomes available in a timely manner.

3.6.2.1 Geochemical Processes. The three predominant geochemical processes affecting radionuclide mobility are: (1) dissolution/precipitation, (2) sorption, and (3) matrix diffusion. These processes are analyzed in the following subsections. Filtration also could be an effective waste isolation process in some cases, and filtration is briefly discussed. Time exerts an important influence on the cumulative release of radionuclides, and time also is discussed in a following subsection.

Radionuclide Dissolution/Precipitation Processes - The combined effects of dissolution and precipitation processes control the solubility or concentration of a given radionuclide in solution. The solution is assumed to be groundwater, either of a composition initially present at the site before repository construction and waste disposal, or of a composition altered due to repository construction and waste disposal operations. Solubility refers to the saturated solution concentration of a radionuclide species in equilibrium with a solid phase containing that radionuclide. If sufficient thermodynamic data is available descriptive of the solid, solution species, groundwater parameters, and thermal evolution of the repository, the solubility may be calculated. Concentration refers to the actual concentration of a given radionuclide in solution as determined by some analytical method. The concentration may be less than the solubility of that radionuclide if the solution is not saturated, or may be greater if supersaturation has occurred. The saturated solution concentration is equivalent to the solubility value for a given solid phase. An apparent concentration limit is the maximum amount of a radionuclide which can be obtained in a solution by experimental methods, and may be equivalent to the solubility value.

The types of data or information needed to analyze the effects of the dissolution/precipitation processes on the transport and release of radionuclides include: (1) groundwater composition, (2) groundwater redox conditions and pH, (3) mineral assemblages and host rock composition along the release pathway, (4) radionuclide solution species, (5) radionuclide particle and colloidal forms, both real and pseudo, (6) dissolution and precipitation reaction kinetics, and (7) radiolysis reactions. Knowledge of the mathematical modeling methodology will also be needed to ensure that the geochemical data obtained is appropriate for the modeling activity.

The groundwater composition, and parameters such as pH and redox conditions, play an important role in controlling the solubility of radionuclide species, and information about these groundwater aspects will be needed. Groundwater composition and parameters may change, relative to initial values, due to reactions with waste package components. Thermal effects resulting from decay heat after closure which could accelerate slow reactions and/or initiate new rock/groundwater reactions will also need to be evaluated. Therefore, the compositions and parameters of all groundwaters in the radionuclide release pathway will need to be considered. Information concerning ions present in the groundwater which could form complexes with radionuclides and thereby increase solubility or hinder sorption will be particularly important.

It is anticipated that radionuclide release through the geologic setting may follow discrete pathways. Therefore, knowledge of the mineral assemblages along the potential release pathways will be needed to understand the rock/groundwater reactions and the radionuclide and/or groundwater component dissolution/precipitation reactions which may occur during migration. Some radionuclides show large differences in solubility or apparent concentration limit with relatively minor changes in groundwater composition and parameters.

Radiolysis reactions in the vicinity of the waste packages may alter the groundwater composition and conditions, or the radionuclide species, as a result of reactions with products of radiolysis of water and air such as hydrogen peroxide or nitric acid. An understanding of radiolytic effects may be needed, particularly during the first few hundred years when fission product decay generates strong gamma radiation which can penetrate the canister and interact with groundwater in the vicinity of the canister.

Alpha radiolysis reactions with groundwater would become important only after canister failure when groundwater comes into contact with the waste form, because alpha radiation will be strongly adsorbed by the canister. Alpha radiolysis reactions could play a significant role in establishing the actinide-element speciation in solution due to the presence of multiple valences and species of actinide elements formed from radiolytic reactions. Therefore, long-term modeling of actinide release rates may require some information regarding alpha radiolysis reactions.

Sorption Process - Radionuclides migrating in groundwater may be retarded, relative to the groundwater flow rate, due to sorption onto solids present in the geologic setting. Sorption refers to any set of geochemical processes that result in the binding of radionuclides to geologic solids. Terms such as ion exchange, adsorption, or chemisorption are sometimes used to identify specific sorption processes. However, sorption reactions are difficult to characterize, and we have chosen not to attempt to discuss subclasses of sorption reactions. The types of data and information needed to analyze the effects of sorption on the transport and release of radionuclides include: (1) mineral assemblages along the release pathway, (2) groundwater composition, (3) groundwater redox conditions and pH, (4) radionuclide species, (5) sorption/desorption kinetics, (6) sorption competition between radionuclides and groundwater species, and (7) sorption isotherms. Knowledge of the mathematical modeling methodology will be needed to ensure that the sorption data obtained is appropriate for the modeling activity.

Radionuclides may be present in groundwater in a number of forms that, in turn, may display different mobilities. Solute species, whether ionic or non-ionic, may be expected to move at the groundwater flow rate unless sorption reactions bind these species to minerals or rock phases adjacent to the release pathway. Because many sorption reactions have at least some aspects of ion exchange phenomena, it may be anticipated that cationic species of radionuclides may be much more strongly sorbed and retarded than anionic or non-ionic species. Therefore, knowledge of the speciation of radionuclide solutes may be considered necessary in order to predict sorption retardation.

Colloidal or particulate forms of radionuclides may exhibit mobilities different from solute forms. Colloidal radionuclides, either as true colloids of radionuclide solid phases or as pseudocolloids of radionuclides carried by sorption or coprecipitation with groundwater or mineral colloids, may be retarded relative to groundwater flow by sorption or filtration processes. Thus, knowledge of the various colloids and particulates which may be present in migrating groundwater, as well as the degree of crystallinity or particle size of radionuclide precipitates, will be necessary information.

Radionuclide speciation is controlled by groundwater composition and parameters such as pH and redox condition. Thus, as for radionuclide solubility, knowledge of these groundwater aspects will be necessary. Radionuclides species may have greatly different sorption coefficients for different minerals. Knowledge of the mineral assemblages along the release pathway and measurement of radionuclide sorption ratios with representative or actual minerals and groundwaters will be essential to supply sorption data supportive of retardation modeling activities.

Retardation of solutes due to the sorption process is a multi-stage process that represents the sum of many sorption and desorption reaction steps between the solid and solution phases. To accurately model the degree of retardation anticipated for a given radionuclide, it may be necessary to measure both the steady-state sorption and desorption ratios and the rates of the sorption and desorption reactions. These measurements must be made under conditions representative of the mineral assemblages and groundwater compositions to be encountered along release pathways. The exact data needed will, in part, depend on the migration modeling methodology selected.

Competition between different radionuclides, or between radionuclides and groundwater constituents, may affect the sorption and desorption ratios for some radionuclides. Also, the effect of radionuclide concentration on the sorption and desorption ratios must be considered. To deal with these aspects of radionuclide sorption, sorption and desorption isotherms may need to be constructed for various groundwater compositions and radionuclide mixtures. Again, the exact data needed will, in part, depend on the migration modeling methodology selected.

Matrix Diffusion Process - Matrix diffusion is defined as the aqueous diffusion of molecules or ions from a water-filled fracture into the groundwater contained in adjacent porous rock. Prediction of the rates of migration of radionuclides through the host rock and the quantities of radionuclides that may be released from a repository will require knowledge of the retardation that may result from matrix diffusion of radionuclides. A number of variables affect matrix diffusion in rock media. These include: (1) fracture aperture, (2) groundwater velocity through fractures, (3) solute concentration gradients between fractures and matrix, (4) degree of matrix saturation with groundwater, (5) matrix porosity, and (6) effective diffusion coefficients for diffusing species. Quantitative knowledge of all these parameters may be needed to accurately assess the possible radionuclide retardation which may result from matrix diffusion. In general, the effects of matrix diffusion are enhanced by: (1) narrow fracture apertures, (2) slow rates of groundwater flow, (3) steep solute concentration gradients between fractures and matrix, (4) complete saturation of the matrix by groundwater, (5) high matrix porosity, and (6) large diffusion coefficients for diffusing species. When fractured rocks have a high sorptive capacity for dissolved species in groundwater, matrix diffusion is largely restricted to comparatively small volumes of rocks adjacent to fractures. Because there are so many different and highly variable physicochemical factors that can influence the nature and extent of matrix diffusion of radionuclides as a retardation mechanism, it may be difficult to predict the significance of matrix diffusion for the anticipated repository performance.

Filtration Process - Filtration is the process whereby particulates are trapped during movement through a porous medium. Filtration may only be a significant radionuclide retardation process in the event that radionuclides can be transported through the geologic setting as adsorbed species on the surface of naturally-occurring particles or particles resulting from waste package/groundwater reactions.

Time - Several aspects of time are important in controlling the release of radionuclides to the accessible environment. Although time is not, strictly speaking, a geochemical process, the effects of time are inextricably intertwined with the geochemical processes discussed above. The important aspects of time with respect to radionuclide transport and release are: (1) radionuclide half-life, (2) groundwater travel time, and (3) regulatory times.

Radionuclides are temporally unstable. Thus, the decay constant (half-life) of the radionuclide, the length of time for travel from the engineered facility to the accessible environment (the product of groundwater travel time and the retardation factor), and the regulatory requirement or repository performance time-frame being modeled all can have a major effect on the cumulative radionuclide releases. Data and information about these temporal aspects of radionuclide transport will be needed. If, for example, the half-life of a given radionuclide is short compared to the travel time to the environment from the engineered facility, then releases of that radionuclide may be inherently minor or negligible. In that case, accurate data and information on the geochemical behavior of this radionuclide may be of minor significance in the release modeling activity.

3.6.2.2 Hydrogeologic Regimes at the Hanford Site. Because groundwater transport is the most credible mechanism that could lead to transport of mobilized radionuclides and release of radionuclides to the accessible environment, the discussion of data and information needs is subdivided below into subsections corresponding to the major hydrogeologic regimes at the Hanford Site.

Flows of basaltic magma have repeatedly erupted over millions of years and cover an extensive area of western Washington. In the Pasco Basin, the basalt depth exceeds 1000 m. Each lava flow forms a discrete horizon in the rock stratigraphy and is characterized by a brachiated flow bottom and flow top which are more permeable and porous than the colonnade or entablature basalt. The flow top and bottom may be saturated withgroundwater. In addition, several periods of extended magmatic inactivity occurred and a weathered surface developed which accumulated extraneous (nonbasaltic or weathered basaltic) materials. These materials were subsequently buried under later basalt flows. These weathered-surface horizons are identified as "interbed strata", and some are now the location of major potable-water aquifers.

Candidate Repository Flow - Water in the flow top or flow bottom may move through fractures or fissures in the repository flow and penetrate the waste package. Rock/groundwater reactions in this horizon affect the composition of the groundwater that flows toward and away from the waste package. The radionuclide source term will be affected by the geochemical conditions and processes in the repository horizon.

Data and information will be needed descriptive of the composition(s) and parameters(s) of groundwater which may be expected to enter the engineered facility and contact the waste packages. To help extend source term predictions over the 10,000-year regulatory time-frame, knowledge of the of the mineral assemblages along groundwater flow paths in the repository flow and how the compositions and conditions may change over time will also be needed. Knowledge of host rock mineralogy and secondary mineralogy associated with fractures and fissures will be important. Radionuclide dissolution and precipitation processes and sorption reactions that could be effective must be evaluated to determine the source term as a function of time at the engineered facility-geologic setting interface. Temperature and pressure will be important parameters. The effect of radiolytic reactions and reactions of methane may be important. The radionuclide solubility or concentration in solution is governed by the difference between the dissolution and precipitation processes in the various regions of the repository flow, and knowledge of the kinetics and steady-state values for these processes will be needed under relevant geochemical parameters. If the DOE chooses to take credit for strongly reducing conditions in the repository flow to limit the solubility of some radionuclides, information of redox conditions will be important. Sorption of radionuclides by the secondary minerals may be important in controlling radionuclide retardation.

Superjacent Basalt Flows - Mobilized radionuclides in migrating groundwater may move into superjacent basalt flows. The geochemistry of these flows may be similar to that for the repository flow, with the principle change being that temperature would decrease over distance from the engineered facility. Groundwater flow likely would be primarily through pre-repository construction fractures and fissures. Matrix diffusion is not likely to be an important retardation parameter in basalt flows.

Data and information will be needed which us descriptive of the radionuclide dissolution/precipitation processes and sorption process. The groundwater composition may change due to contact with fracture-lining secondary minerals. Sorption of radionuclides by these minerals may be different than in the repository flow. Methods for measuring and modeling sorption under fracture-flow conditions may need to be developed. Because the release pathway(s) have not been established for the Hanford Site, it may not be possible to predict all the needed data and information at this time.

Interbed Strata - The interbed strata constitute geologic setting zones which are quite different from the basalt flows. The aquifers are primarily in contact with minerals derived from sediments and weathered basalt, unaltered basalt minerals may be generally absent or present in minor quantities, and the groundwater may be flowing laterally through the strata toward the accessible environment. Modeling the mobility of radionuclides in these strata likely will be important in predicting repository performance. However, release pathways have not been determined for the Hanford Site, and it may not be possible to identify all the data and information needs for these strata at this time.

The volume of groundwater is much higher in this zone than in subjacent basalt flows. Also, the rates of lateral movement of groundwater may be greatly increased in these strata while rates of upward movement may be greatly diminished. Ingressing radionuclide-bearing groundwaters would be highly diluted by mixing with the radionuclide-free groundwaters that flow through these strata. Also, clay-rich regions of these strata may provide significant radionuclide sorption capability. As in the cases of the subjacent basalt flows, data and information will be needed to describe the radionuclide solubility or concentration, and for the sorption and desorption reactions. Existing experimental and modeling methodology may be adequate to describe sorption in the saturated zone. The groundwater composition and conditions may change in this zone due to dilution and reaction with a different mineral assemblage. Information descriptive of the groundwater composition and conditions and their affects on radionuclide solubility and sorption reactions likely will be needed. Matrix diffusion of radionuclides could be a potentially significant retardation process in these strata. At least, matrix diffusion is more conceivable as a process in these strata than in the basalt flows. Considering the total effect of these geochemical processes, it is possible that this zone could provide appreciable retardation for mobilized radionuclides and, thus, data and information needed to evaluate retardation will be important.

3.6.3 Methods, Strategies, and Approaches to Acquire the Needed Data and Information Geochemical Processes

3.6.3.1 Radionuclide Dissolution/Precipitation Processes

(1) groundwater composition - analysis of samples of *in situ* groundwaters and groundwaters altered by thermal/radiolysis effects due to emplacement of waste and engineered facility components; chemical analyses for major and minor components by ICP, AA, NAA, and wet chemical methods for both inorganic and organic constituents

(2) groundwater redox condition and pH - analysis of samples of *in situ* groundwaters and groundwaters altered by thermal/radiolysis effects due to emplacement of waste and engineered facility components; pH measurement with standard electrodes, Eh measurement with platinum electrode, estimation of system Eh by measurement of element couples [e.g., Fe(II)/Fe(III)] in solution, calculation of system Eh from data on mineral assemblages

(3) mineral assemblages and host rock compositions along the release pathway - recovery of samples from drill holes and exploratory shaft; analysis by physical methods (XRD, SEM) and chemical methods to identify major and minor minerals; important to do cross section of samples to identify minerals in direct contact with flowing water

(4) radionuclide solution species - identify solution speciation (valence, complexation, hydrolysis) by spectroscopic, lacer-induced photoelectron spectroscopic, and electrochemical methods of radionuclides dissolved in *in situ* groundwaters and groundwaters altered by thermal/radiolysis effects due to emplacement of waste and engineered facility components

(5) radionuclide particle and colloid forms - identify particles/colloids in *in situ* groundwaters, groundwaters altered by thermal/radiolysis effects due to emplacement of waste or engineered facility components by Debye light scattering, sequential filtration techniques; chemical analysis of recoverable particles/colloids

(6) dissolution and precipitation reaction kinetics - measurement of both major and minor mineral/host rock components, and radionuclide

concentrations in *in situ* groundwaters and groundwaters altered by thermal/radiolysis effects due to emplacement of waste and engineered facility components; AA, NAA, ICP, wet chemical, and spectroscopic methods

(7) radiolysis reactions - chemical analysis for radiolysis reaction products of groundwater such as H_2O_2, organic acids, and changes in radionuclide speciation

3.6.3.2 Sorption Process.

(1) mineral assemblages along the release pathway - see above

(2) groundwater composition - see above

(3) groundwater redox condition and Eh - see above

(4) radionuclide species - see above

(5) sorption/desorption kinetics - both batch contact and column chromatographic methodology should be employed to study radionuclide sorption and desorption reactions as a function of time; test conditions and parameters should span the ranges anticipated in the repository over time; groundwaters and substrates should include those expected in the engineered facility and along the release pathway

(6) sorption competition between radionuclides and groundwater species - sorption/desorption kinetic studies (see 5 above) should have an expanded test matrix to include variable concentration of groundwater species

(7) sorption isotherms - batch contact methodology should be employed with the test matrix (see 5 above) including various concentrations of radionuclides to allow construction of sorption isotherms

3.6.3.3 Matrix Diffusion Process.

(1) fracture aperture - both the average and range of fracture apertures should be measured by down-hole and direct methods from the exploratory shaft

(2) groundwater velocity through fractures - measured from the exploratory shaft

(3) solute concentration gradients between fractures and matrix - measured in laboratory experiments

(4) degree of matrix saturation with groundwater - measured by heating and weighing samples recovered from air-sparged drill holes and from the exploratory shaft

(5) matrix porosity - measured by BET and mercury infusion techniques on samples recovered from drill holes and from the exploratory shaft;

(6) effective diffusion coefficients for diffusing species - radionuclides allowed to diffuse from groundwater samples into wafers or pieces of matrix recovered from drill holes and exploratory shaft; depth of penetration determined as a function of time

3.6.3.4 Filtration Process.

- removal-from-solution of radionuclides onto colloidal or dispersed particulates by flow through matrix samples recovered from drill holes and exploratory shaft

3.6.4 Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue

(TO BE COMPLETED BY SEPTEMBER 30)

DRAFT 08/06/87

MR-287-11
nn/nn/87

MEETING REPORT

TITLE: NRC Data Review of Information on BWIP and PNL Experiments Using Hydrazine to Establish Reducing Redox Conditions in Radionuclide Sorption Experiments, meeting held at PNL, Richland, WA, on July 21-22, 1987

ATTENDEE: A. D. Kelmers

AUTHOR: A. D. Kelmers

PROJECT TITLE: Technical Assistance in Geochemistry

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MARTIN MARIETTA ENERGY SYSTEMS, INC.

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)/ NRC # 50 19 03 01

SYNOPSIS

A data review meeting was held at Richland, WA, on July 21-22 to examine records of the experiments performed by PNL and BWIP staff which generated the BWIP data base of radionuclide sorption information under reducing redox conditions. In these experiments in the past, primarily during 1980 and 1981, hydrazine was added to rock/groundwater mixtures to produce a strongly reducing condition. Work performed under the NRC B0290 project at ORNL (reported in NUREG/CR-3851, Vol. 1, 1984) suggested several concerns relative to both the suitability of the experimental methodology and the applicability of the test results for site characterization or performance modeling applications. These concerns were then formalized in a draft NRC Site Technical Position (STP) on the use of hydrazine. Following the period of public comment on the draft STP, a response was received by the NRC from DOE/Hanford which challenged or attempted to refute all six of the concerns presented in the draft STP (letter from Anttonen, February 23, 1987). Therefore, a data review meeting was arranged to allow the NRC, NRC contractors, and affected Indian tribes and states, to examine the original experimental records of the PNL amd BWIP radionuclide sorption tests involving hydrazine. Prior to the meeting, the NRC submitted a detailed

data requests to BWIP (Attachment 1 of this Meeting Report). Six NRC concerns were listed, and a total of 17 data and information needs were identified. The data and information needs represented technical items which could help resolve the concerns.

At the beginning of the meeting, a schedule was distributed (Attachment 2) and the ground rules for conduct of the meeting were established (Attachment 3). An extensive collection of the pertinent original laboratory records was made available by BWIP, and the relevant citations in the records were cross referenced by the 6 NRC concerns and the 17 data and information needs (Attachment 4). The BWIP and PNL staff obviously had spent considerable time in preparation for the data review meeting.

The six concerns expressed in the NRC draft Site Technical Position are restated below, along with a brief summary of the author's evaluation of (1) the position taken in the Anttonen letter, (2) the PNL and BWIP information made available at the data review meeting, and (3) possible means of resolving outstanding concerns.

NRC Concern 1 - Experimental redox conditions established by hydrazine may not reflect site conditions

The Anttonen response stated that the addition of hydrazine was never meant to simulate repository redox conditions, but, rather, to easily form reduced species of radionuclides. The argument continues that, once formed, the behavior of reduced radionuclides in laboratory tests can be used to gain information about radionuclide retardation in the repository. It appears to have been assumed that sufficient information exists in the literature to predict the species formed by hydrazine reduction.

Little work was cited at the data review meeting which compared the redox condition established by hydrazine and the expected *in situ* redox condition. Nor were direct chemical methods employed to assure that reduced radionuclide species resulting from the addition of hydrazine (or the kinetics for the formation of those species) were similar to those resulting from basalt-radionuclide reactions. Inferential and indirect evidence was apparent employed as the experimental rational.

Resolution of this concern could require considerable additional laboratory- and field-scale experimentation to prove that (1) reduction by hydrazine and by basalt lead to the same radionuclide species and (2) the Eh or redox condition of the laboratory tests with hydrazine and of the field conditions poised by basalt/groundwater chemistry are known and comparable, if not identical.

NRC Concern 2 - Hydrazine dissociates to release OH^- ions, thus the test pH may not reflect site conditions

The Anttonen response states that the use of HCl to readjust the groundwater pH after hydrazine addition is a valid method.

Based on documents inspected at the meeting, is became apparent that PNL and BWIP work used different experimental techniques. PNL tests did not allow for readjustment of the pH by the addition of acid, while in BWIP experiments HCl was added after hydrazine addition to reestablish the groundwater pH. It was not clear at the data review meeting what affect this methodology difference may have on interpretation or comparison of results from PNL visavis BWIP.

The Anttonen response did not address the fact that the PNL experiments did not employ pH adjustment after hydrazine addition. A thorough evaluation of the resulting pH of the PNL and BWIP experiments, and of the relationship of these pH levels to repository conditions could be required to resolve this concern.

NRC Concern 3 - Hydrazine may react with bicarbonate to form carbamate ions.

The Anttonen response recommended that this concern by dropped.

This concern was not addressed at the data review. The NRC has indicated that this concern will probably be dropped from a revised draft Site Technical Position.

This concern should be resolved by elimination from a revised STP.

NRC Concern 4 - Reactions may occur between hydrazine and rock or mineral surfaces, thus the test components then may not be representative of site conditions

The Anttonen response attempted to dispose of this concern by citing evidence from various tests where the sorption results did not show obvious changes in sorption behavior due to the addition of hydrazine. Such evidence was inferred to show that hydrazine does not attack or alter minerals/rock surfaces. A distinction between radionuclides sorbed by ion exchange and by surface complexation was attempted. These proposed mechanisms were not rigorously defined, nor were statements confirmed that "key" radionuclides are sorbed only by ion exchange mechanisms that are not adversely affected by the addition of hydrazine.

Information made available at the data review suggests that neither PNL nor BWIP considered possible reactions between hydrazine and rock or mineral components. Failure to consider such reactions may represent a significant deficiency in evaluating the usefulness of the sorption data. Evidence cited previously by the NRC shows that appreciable chemical reactions can occur between hydrazine and various minerals and rocks.

Considerable additional experimental work could be required to prove that significant reactions do not occur between hydrazine and rock surfaces or minerals. Additional work also could be needed to understand the sorption processes for various important radionuclides if a mechanistic explanation of sorption processes is to be attempted.

NRC Concern 5 - Use of exogenous homogeneous reductants such as hydrazine may not simulate repository conditions where heterogeneous rock/groundwater reactions may dominate the system.

At the data review, this concern was combined with concern 1.

NRC Concern 6 - Reaction of hydrazine with plastic tubes; thus, the resulting conditions may no longer be representative of site conditions

The Anttonen response stated that this concern was irrelevant and should be eliminated from the STP.

The information made available at the data review clearly showed that both PNL and BWIP were aware of the serious reactions occurring between hydrazine and polycarbonate tubes, and that use of these tubes was stopped. However, it did not appear that any effort had been made to identify data obtained in polycarbonate tube tests that could be questionable and then expunge such data from the radionuclide sorption data base. It was stated at the data review meeting that the radionuclide data base has not been revised or updated since 1983, and that the 1983 data base will be used for the BWIP Site Characterization Plan document to be issued this fall. Also, no experimental investigation of the possible reactions of hydrazine with the polyethylene ot polypropylene containers used in later experiments was see at the data review.

Resolution of this concern, with respect to the existing data, would require a better understanding of which hydrazine-based sorption data came from tests in polycarbonate tubes. Some aspects of the BWIP information seem not totally consistent with respect to the composition of the test apparatus employed. Additional experimental work would be needed to reach an unambiguous evaluation of the suitability of other plastics used in some later BWIP and PNL experiments.

RECOMMENDATIONS

It is recommended that a Workshop involving BWIP staff and all interested parties be held to address the broader issue of how to simulate, approximate, or reproduce in laboratory experiments the reducing redox conditions expected in the engineered facility and the far-field. The work using hydrazine, which was the subject of the data review, exemplifies the difficulties to be encountered if the experimental methodology is not above scientific reproach. It would seem to be in the best interests of all parties to explore and attempt to reach a consensus on the experimental methodology to be used to establish reducing conditions in future laboratory work.

EVALUATION OF INFORMATION IN CITED DOCUMENTATION RESPONDING TO THE DATA AND INFORMATION NEEDS

During the two-day period of the meeting, the author read and evaluated most of the indexed citations and entered marginal notes on his copy of Attachment 4. The following section of this Meting Report constitutes an expansion of those marginal notes. The NRC submitted a number of written data clarification questions at the meeting (Attachment 5). These are briefly addressed in a later section. At the conclusion of the meeting, the NRC Project Manager, and BWIP and DOE managers drafted a joint statement. This statement is supposed to be distributed subsequent to the meeting to the participants, and is not included in this Meeting Report.

RESPONSE BY PNL

NRC Concern 1 - Experimental redox conditions established by hydrazine may not reflect site conditions

Data and Information Needs (see Attachment 4) -

1a - This citation describes the redox titration of some redox buffers used in a few tests; not relevant to the concern.

1b - Standard reference to Ag/AgCl half cell potential.

2,3,4a - Citation of unreported data; data not available to public.

2,3,4b - Reference to work by others on technetium reduction by iron.

2,3,4c - Results showed that most radionuclides were removed as precipitates under reducing conditions, rather than by sorption; raises questions as to cause of removal from solution for radionuclides in many tests.

2,3,4d - Technetium valence apparently responded to Eh changes on basalt surfaces while the Pt electrode did not; raises questions as to usefulness of Eh measurements.

2,3,4e - Interesting new work (1986) employing x-ray photoelectron spectroscopy and x-ray diffraction techniques to characterze sorbed and precipitated radionuclide species; would be interesting to see additional results of these promising technique.

5a - Presence of selenium metal identified by x-ray diffraction.

5b - Sorption experiments in polycarbonate tubes; tube degradation noted; not obvious that results were discarded because of tube attack by hydrazine.

6a - Not evaluated.

6b - This citation is a general listing of six data notebooks; not useful to the data review because specific items not identified.

NRC Concern 2 - Hydrazine dissociates to release OH^- ions; test pH may not reflect site conditions

Data and Information Needs (see Attachment 4) -

7 - PNL did not readjust groundwater pH after the addition of hydrazine; this is in contrast to BWIP work where HCl was used to readjust the pH; this may be a significant different in the technique between BWIP and PNL.

NRC Concern 4 - Possible reactions between hydrazine and rock or mineral surfaces; test components then may not be representative of site conditions

Data and Information Needs (see Attachment 4) -

8a - Reduction of selenate by copper metal; not relevant to the concern.

8b - More data on reduction of selenate and pertechnetate by copper metal; not relevant to the concern.

8c - Reduction of Pu(VI) by both hydrazine and dithionate.

8d - Technetium and actinide sorption onto magnetite and hematite; not relevant to the concern.

8e - Inactivation of basalt by exposure to air; not relevant to the concern.

9a - Lead sorption with and without hydrazine; not relevant to the concern.

9b - More lead and zirconium sorption; see 9a.

10a through 10j - It was difficult to see the connection between the cited data and the NRC concern; it appeared that underlying assumptions were not identified or spelled out.

11,16a - Reaction between basalt and hydrazine in distilled water; disagreed with the stated conclusions.

NRC Concern 6 - Attack of hydrazine on plastic tubes; thus, resulting conditions may no longer be representative of site conditions

Data and Information Needs (see Attachment 4) -

12,15a - Documented use of glass Wheaton bottles; not relevant to the concern.

12,15b - Studied release or organics from plastic tubes into distilled water; not relevant to the concern.

13 - Statement that PNL did not use polycarbonate tubes at 85 °C is correct, however PNL did use polycarbonate tubes at 23 and 65 °C and did note degradation due to reaction with hydrazine.

14 - Tests in polycarbonate tubes were not duplicated in new plastic or glass containers.

RESPONSE BY BWIP

Data and Information Needs (see Attachment 4) -

1 - Conventional calculation of Eh from standard half cell potentials.

2 - Direct methods were not used to determine species of reduced radiuonuclides; citations are to tests in polycarbonate tubes.

3 - Direct methods were not used to determine the kinetics of postulated hydrazine-radionuclide reactions.

4 - Citation references 2 and 3 (see above).

5 - Direct methods were not used to determine reaction products of selenite and hydrazine.

6 - No oxygen-radionuclide reactions were studied.

7 - HCl was used to readjust the groundwater pH after the addition of hydrazine; this is in contrast to PNL methods, see above.

8 - Only the sorption of selenium, added to the tests as selenite, was studied with hydrazine and other reductants.

9 - No relevant discussion of ion exchange vs surface complexation reactions.

10 - Citation references 9 (see above).

11 and 12 - Citation states see PNL work

13 - Cited tests of backfill in Teflon tubes does not repeat earlier work with sandstone in polycarbonate tubes.

14 - No analysis of sorption data obtained in polycarbonate tubes to discard potentially invalid data.

15 - Citation references 12 (see above).

16 - Work on technetium sorption is not relevant to the concern.

17 - Laboratory notebook references cited are only to experiments in polycarbonate; the references do not resolve the uncertainties concerning published data stated to have been obtained in polyethylene tubes.

DATA CLARIFICATION QUESTIONS

1 - Is SD-BWI-DP-001 (1983) still the current sorption data package? BWIP answered that this data package has not been updated and will be used to support the BWIP Site Characterization Plan to be issued this fall. Revision of this data package is a project milestone for FY 1988.

2 - Requested a copy of BWIP internal progress report for January 1981. A copy was made available.

3 - Requested any additional information showing how the various reported Eh values were measured or calculated. Response suggested that all data had already been made available.

4 - Requested additional information on direct studies of hydrazine reactions with sorption substrates. The response appeared to suggest that the BWIP had not considered such reactions to be important.

5 - Requested additional information on hydrazine -- test-container reactions. Response was that hydrazine was not believed to be adsorbed.

6 - Requested additional information explaining difference between ion exchange and surface complexation sorption. Response seemed to suggest that all available information has been made available. (It was not clear to the author how these two supposedly different sorption mechanisms are defined or differentiated.)

7 - Questioned the basis for the difference between BWIP and PNL approaches of use/non-use of acid to reestablish the groundwater pH after hydrazine addition. Only PNL experimental staff was present at the review meeting. PNL staff could not explain the difference and seemed to have had little contact with BWIP experimental staff.

8 - Questioned apparent anomalies between BWIP notebooks on tests in which polycarbonate tubes were employed (and attack by hydrazine noted), and publications stating tests were done in polyethylene. BWIP is supposed to respond to this in writing later.

ATTACHMENT 1

NRC DATA REQUEST FOR BASALT-SITE
HYDRAZINE DATA REVIEW

GENERAL:

In addition to the following list of specific data, any other data that would be useful for resolving our concerns should be brought to our attention and made available.

SPECIFIC:

A. NRC Concern 1: Hydrazine can exhibit both reduction reactions and oxidation reactions which have widely different standard potentials. Thus experimental redox conditions may not reflect site redox conditions.

A1. Issue(s)

- Redox condition or Eh established by the addition of hydrazine.
- Rate of reduction of radionuclides by hydrazine.

A2. Basis For Concern

- Various BWIP publications give Eh values of +0.2, +0.5, and +0.6 volt as representative of air-saturated redox conditions, and Eh values of -0.4 and -0.8 volt as representative of reducing redox conditions with hydrazine present. The reducing tests are at various pH's, temperatures, and hydrazine concentrations (both 0.05 and 0.1 M), so possibly these test parameters are significant in the calculations and account for the different Eh values reported. We do not understand, however, why such a range of Eh values are given in different reports for what seem like equivalent oxidizing rock groundwater systems.

ADK 3

- The concept of representing the redox state of a system by a single Eh value is a strictly hypothetical concept which assumes that all redox reactions are at equilibrium with each other and, therefore, that the concentrations of the reduced oxidized species of the various redox couples can be calculated from a single master variable, the system "Eh". In reality, it is rarely the case that a master Eh can be applied to any geochemical system because all redox couples are seldom simultaneously at equilibrium due to reaction kinetics and activation energy barriers for some reactions. Therefore, if the stated objective of the BWIP work employing added hydrazine is to study the sorption of reduced states of radionuclides such as technetium and neptunium, it cannot be assumed that the reduced species are actually formed solely on the basis of a calculation for some Eh value. Nor can it be assumed, based on information in the chemical literature obtained under other test parameters (e.g., pH, supporting electrolyte, radionuclide concentration), that the radionuclide reduction reactions reported in the literature with hydrazine will actually occur in the rock-groundwater systems of interest.

- Although the sorption ratio for some radionuclides is observed to be greatly enhanced by the addition of hydrazine, this observation does not unambiguously prove that reduced radionuclide species were formed or that reduced species are more strongly sorbed than oxidized species. For example, the surface of the minerals could be affected or altered by the hydrazine in such a way that the sorption of some radionuclides is affected while others are not. Or, it might be that hydrazine reduces Fe(III) to Fe(II) on or near the mineral surface and that the greatly enhanced concentration of Fe(II) on the mineral surface causes a chemical reaction with some radionuclides to form insoluble products rather than result in sorption of reduced ionic radionuclide species. The processes which control sorption are often quite complex; therefore, it cannot be assumed that observations for one radionuclide (or a small group of radionuclides) can be generalized and applied to other radionuclides.

ADK (4)

- The three questions posed by Anttonen (1987) go to the heart of the issue of the appropriateness or applicability of tests employing hydrazine to gather radionuclide sorption data descriptive of the BWIP candidate repository site. These questions are: "... (1) are the reduction reactions fast enough to be useful in these experiments? (2) what are the reaction products? and (3) are the reaction products the same as those expected in a basalt-groundwater environment?"

- In Anttonen (1987), a statement is made that hydrazine reacts rapidly with key radionuclides and maintains the desired lower oxidation states over the course of the sorption reactions. This is an important statement because, if substantiated, it helps justify the use of hydrazine in sorption experiments. In the BWIP publications available to us, we have not seen the results of kinetic experiments which identify the radionuclide species formed by the proposed reactions with hydrazine and the rate at which these are formed. Conclusions about radionuclide reduction and the rate of reduction seem to be based on experimental evidence of increased sorption distribution coefficients for the radionuclides. To some extent, this seems like circular logic; i.e., hydrazine is added because it is expected to reduce radionuclides and increase sorption, thus, when increased sorption is observed after the addition of hydrazine, it is concluded that radionuclide reduction has occurred and that radionuclide reduction is the only significant reaction that has occurred as a result of the addition of hydrazine to the rock-groundwater system.

- Various BWIP publications contain apparent contradictory statements concerning the reaction of hydrazine with selenate anion and the identify of the product formed. Some of the references state that it is reduced to selenium metal, while others state that it remains anionic.

- Hydrazine is reported to react more rapidly with radionuclides than does dissolved oxygen in the rock-groundwater system, thus keeping the radionuclides in the desired reduced state (Barney et al., 1983).

A3. Request for Supporting Data

We would like to review all laboratory procedures, data note books, laboratory records, tables or plots of data, calculational methodology and calculated numbers, computer print-out, records of data analysis and evaluation, and other relevant documentation relating to the following:

(1) - The calculations which were used to obtain the Eh values reported for both oxidizing and reducing redox conditions in the various BWIP sorption experiments.

(2) - Experimental data that substantiates by direct chemical analysis (e.g., spectrophotometry, electrochemistry, laser-induced photo-acoustic spectroscopy) that radionuclides stated to be reduced by hydrazine are actually presence in the groundwater-rock systems as the lower-valence ionic species identified in Table I of Anttonen 1987.

(3) - Evidence that answers the questions raised in the last paragraph of the first page of Anttonen (1987) relative to the validity of the experimental methodology employing hydrazine. These questions are: "... (1) are the reduction reactions fast enough to be useful in these experiments? (2) what are the reduction products? and (3) are the reaction products the same as those expected in a basalt-groundwater environment?"

(4) - The experimental data, other than indirect sorption data, that measured the rate of reaction between hydrazine and radionuclides, and identified the reduced radionuclide species formed as a function of time.

(5) - The experimental data on the rate of reduction of selenate anion by hydrazine in rock-groundwater systems and identification of the selenium-containing compound(s) formed.

ADK (6)

(6) - Any experimental data on the <u>relative</u> rates of reaction of hydrazine with radionuclides as compared to the rate of reaction with dissolved oxygen in rock-groundwater systems.

B. <u>NRC Concern 2</u>: Hydrazine hydrate dissociates to release hydroxide ions. Thus, experimental pH conditions may not reflect site pH conditions.

B1. <u>Issue(s)</u>

- Effect of added hydrazine on the pH of test solutions

B2. <u>Basis for Concerns</u>

- Hydrazine is a basic reagent and the addition of N_2H_4 increases the pH of poorly-buffered aqueous solutions such as groundwaters. Anttonen (1987) states that HCl was used to adjust the groundwater pH after the addition of hydrazine in BWIP experiments. In the BWIP publications available to us, only in a footnote to Table I in Barney (1984), and in Barney et al., (1985) are direct references made to the use of HCl to readjust the groundwater pH. Other publications from 1981 through 1984 simply mention the addition of hydrazine.

B3. <u>Data/Information Needed to Review Concern/Issue(s)</u>

We would like to review all laboratory procedures, data notebooks, laboratory records, tables or plots of data, calculational methodology and calculated numbers, computer print-out, records of data analysis and evaluation, and other relevant documentation relating to the following:

(7) - The use of acid (or other methods) to reestablish the pH of the groundwater after the addition of hydrazine.

C. <u>NRC Concern 3</u>: Hydrazine can react with the bicarbonate anion to form the carbamate anion. Thus, the experimental groundwater may no longer be representative of site groundwater conditions.

ADK (7)

C1. Issues

None. DOE has presented information that the formation of hydrazine carbamate is unlikely. We concur that little strong evidence exists to support the NRC concern that hydrazine carbamate would form in dilute solutions.

C2. Basis for Concern

- No experiments have been conducted to explore this reaction.

C3. Data Information Needed to Review Concern(s)/Issue(s)

- None. This concern will be evaluated based on existing information/data.

D. NRC Concern 4: Hydrazine is reported to disrupt the mineral structure of clays, and disaggregate rock. Thus the rock/mineral components of the experiments may no longer represent those found under site conditions.

D1. Issues

- Interaction/Interference of hydrazine with sorption reactions and/or with rocks or minerals.

D2. Basis for Concern

- The statement is made in Anttonen (1987) that sorption distribution coefficients are the same for reduced radionuclides whether or not hydrazine is present. The BWIP publications available to us do not contain the results of an experimental investigation comparing radionuclide sorption of species reduced by hydrazine and reduced by other methods. Such information could be important in supporting the validity of the use of hydrazine.

ADK (8)

- In the BWIP publications available to us, there is an attempt to differentiate between radionuclide sorption by ion-exchange reactions and sorption by complexation with oxygen ligands on the mineral surface. The first mechanism, ion exchange, seems to be invoked in the cases of radionuclides such Cs, Sr, and Ra which are not reduced by hydrazine but show decreased sorption in the presence of hydrazine, while the second, complexation, is invoked in the cases of radionuclides such as Pb, Am and Zr which are not reduced by hydrazine and do not show a change in sorption in the presence of hydrazine. It is not clear, from the BWIP publications available to us, how the distinction between ion exchange and surface complexation reactions is being made.

- According to Anttonen (1987), essentially none of the radionuclides considered 'key' are sorbed by ion exchange. This is a potentially important statement. Numerous BWIP publications describe the competition of NH ions with radionuclide sorption of certain ions assumed to be sorbed by an ion exchange mechanism. In the BWIP publications available to us, we have not identified results of an experimental investigation of the sorption mechanism for the key radionuclides.

- The results of a recent investigation of the interaction of hydrazine and soils (Hayes et al., 1982) seem particularly relevant to the issue of hydrazine interaction with sorbing minerals in the BWIP experiments with basalts or interbed materials. The abstract of that report is quoted:

"Studies have demonstrated that at high pH (pH = 8) in the solution phase, colloids catalyze hydrazine degradation. This catalysis is particularly dependent upon the exchangeable metal cations held by the colloids, and exceeds that of equivalent solutions of metal cations alone. Hydrazines can be strongly or weakly sorbed by soil colloids in essentially unchanged forms, or can be irreversibly chemisorbed. Reversible ion-exchange is the main mechanism of hydrazine/clay interaction at low pH (pH = 4). Insoluble iron-and aluminum-hydrous oxides form on the surface of suitably charged clays at high pH, and these bind large amounts of hydrazines by strong hydrogen-bonding forces and by hydrazination of cationic species. Such binding partially destabilizes hydrazine toward thermal degradation. The results for synthetic goethites resemble those for iron(III) montmorillonite, but interactions are larger per gram of colloid. Reduction of iron(III) to iron(II) occurs, and an iron(II)/hydrazine coordination complex forms which deactivates surfaces at high pH, but is soluble at low pH. Hydrazines react with humic colloids by chemisorption, by ion-exchange, and by hydrazination of strongly polarizing cations. The reactivity of humates is determined by their exchangeable metal cations, and by the pH, which both affect their penetrability and solubility. Clay colloids and goethite react strongly with hydrazines from the vapor phase. Results show that hydrazine can compete well with water for interaction sites. The presence of water also determined the products of thermally induced degradation of sorbate molecules. Preliminary results from whole soil/hydrazine experiments show the large capacity of different soil types for interaction with hydrazine. A copper(II)-treated, aerated soil is highly effective in degrading applied hydrazine."

D3. <u>Data/Information Needed to Review Concern/Issue(s)</u>

We would like to review all laboratory procedures, data notebooks, laboratory records, tables or plots of data, calculational methodology and calculated numbers, computer print-out, records of data analysis and evaluation, and other relevant documentation relating to the following:

(8) - The results of any direct comparisons of the sorptions of radionuclides reduced by hydrazine with the sorption of the same radionuclides reduced by other means.

(9) - The results of experimental investigations that differentiate between ion-exchange and surface complexation mechanisms for the sorption of radionuclides which are not reduced by hydrazine.

ADK (10)

(10) - The results of experimental investigations which identify the sorption reactions of 'key' radionuclides and establish that they are not sorbed by an ion exchange mechanism.

(11) - The results of studies of the interactions of hydrazine-containing groundwater with basalts or interbed materials to look for reactions between hydrazine and mineral constituents. In particular, studies to see if hydrazine undergoes reversible sorption or is irreversibly sorbed onto clays (or other minerals/materials) which are believed to bind radionuclides by ion exchange processes.

E. NRC Concern 5: The chemistry of basalt rock/groundwater systems seems to be primarily dominated by the rock components. Therefore, reactions leading to radionuclide removal from solution by sorption or precipitation must involve hetergenaous reactions between basalt solid surfaces and radionuclide species in solution. Thus, the addition of hydrazine (or any exogenous reducing chemical) seems likely to result in homogeneous solution reactions involving radionuclides not expected under site conditions.

E1. Issue(s)

- Redox condition of Eh established by the additions of hydrazine

E2. Basis for Concern(s)

Same as DSTP Concern 1.

E3. Data/Information Needed to Review Concern/Issue(s)

Same as DSTP Concern 1.

F. NRC Concern 6: Hydrazine is a very aggressive chemical and reacts with plastics in the experimental apparatus. Thus, extraneous reaction products could complicate the interpretation of experimental data to the

ADK (11)

point that the results may no longer represent site conditions or reactions.

F1. Issue(s)

- Interaction of hydrazine with experimental containers, and the stability of hydrazine during tests.

F2. Basis for Concern

- According to Anttonen (1987), there was no evidence for reaction with Teflon, glass, polyethylene, and polypropylene containers. Obviously, use of an inert container is a prerequisite to the successful conduct of any experiment. The results of an experimental investigation to identify suitable containers for radionuclide sorption reactions in rock-groundwater systems containing hydrazine is not in the BWIP publications available to us.

- Much of the earlier BWIP work to measure radionuclide sorption data was conducted in polycarbonate tubes. In at least two BWIP publications (Barney 1982a; Barney 1982b) recommendations were made that the work with selenium, technetium, uranium, and neptunium at 85°C should be repeated due to evidence of hydrazine attack on the containers. We are unable to tell from an examination of the BWIP publications available to us if these experiments were explicitly repeated.

- We have assumed that, following the discovery by BWIP that hydrazine may have reacted with the polycarbonate tubes used in much of the earlier sorption experiments, the earlier data was reexamined and any questionable radionuclide sorption values expunged from the sorption data base. We have not seen reports of such a reevaluation in the BWIP publications available to us.

- The more recent BWIP radionuclide sorption work in the presence of hydrazine has been conducted in a variety of containers. In the BWIP

ADK (12)

publications available to us, we have not seen an explanation of the rationale for the use of different containers.

- Hydrazine is well known to be unstable and decompose in the presence of many materials, although pure solutions of hydrazine in water may be stable for long periods of time. The decomposition of hydrazine may be catalyzed by the presence of many different materials. The BWIP publications available to us do not contain reports of analyses of the hydrazine concentration of the groundwater solutions, or analyses for hydrazine concentration after completion of the sorption experiments. Proof that the hydrazine did not decompose during the experiments seems important because the hyrazine in the groundwater establishes the redox condition or Eh value. Recent work (Hayes et al., 1982) showed that hydrazine decomposes in the presence of soil constituents, and that this decomposition is catalyzed by the presence of metal cations. The decomposition is also thermally accelerated.

F3. Data/Information Needed to Review Concern/Issue(s)

We would like to review all laboratory procedures, data notebooks, laboratory records, tables or plots of data, calculational methodology and calculated numbers, computer print-out, records of data analysis and evaluation, and other relevant documentation relating to the following:

(12) - The experiments which established that Teflon, glass, polyethylene, and polypropylene containers do not interact with hydrazine in groundwater solutions, or that the containers do not affect the hydrazine-radionuclide reactions over the times employed in the longest sorption experiments at room temperature or evaluated temperatures.

(13) - The repeated experiments, as recommended in BWIP publications, of the tests with selenium, technetium, uranium, and neptunium in hydrazine-containing rock-groundwater systems at 85°C conducted in polycarbonate tubes.

ADK (13)

(14) - The review and analysis of the hydrazine work conducted in polycarbonate tubes to determine which sorption data was unaffected by the experimental apparatus, and thus the data could be kept in the sorption data base, and which sorption data was expunged from the data base due to either evidence that reaction with the experimental apparatus may have invalidated the data or uncertainty over the validity of the sorption data due to use of polycarbonate tubes and the possibility of reactions with the container.

(15) - The experimental rationale and demonstration of resistance to attack by hydrazine which supports the use of a wide variety of containers (serum bottles, polyethylene bottles, Wheaton serum bottles, Teflon PFA vials with screw caps) reported in recent (1983 and later) BWIP publications.

(16) - The results of hydrazine analyses which demonstrated that hydrazine was stable and did not decompose due to reaction with the containers and other test components in the rock-groundwater mixtures at room temperature or elevated temperatures over the times employed in the longest sorption experiments.

(17) - The laboratory procedure and records/data for the various tests that support Figure 1, and Table III and VII presented in Barney 1983; Figure 1, and Table III and VII, presented in Barney 1984; Figure 1 and 3, and Table 2 and 7 presented in Barney 1982a; and Figure 1 and 3, and Table 2 and 7 presented in Barney 1982b.

ADK (14)

References

Anttonen (1987) - Letter (87-LES-27) and attachment from J.H. Anttonen, Hanford Operations Officer, U.S. Department of Energy, Richland, WA, to J.J. Linehan, Division of Waste Management, U.S. Nuclear Regulatory Commission, Washington, DC, February 23, 1987.

Barney (1982a) - G.S. Barney, Radionuclide Sorption of Columbia River Basalt Interbed Materials, RHO-BW-SA-198 P, Rockwell Hanford Operations, Richland WA, May 1982.

Barney (1982b) - G.S. Barney, FY 1981 Annual Report Radionuclide Sorption on Basalt Interbed Materials, RHP-BW-ST-35 P, Rockwell Hanford Operations, Richland, WA, October 1982.

Barney (1983) - G.S. Barney, Radionuclide Sorption and Desorption Reactions with Interbed Materials from the Columbia River Basalt Formation, RHO-BW-SA-291 P, Rockwell Hanford Operations, Richland, WA, March 1983.

Barney (1984) - G.S. Barney, "Radionuclide Sorption and Desorption Reactions with Interbed Materials from the Columbia River Basalt Formation," pp. 3-23 in Geochemical Behavior of Disposed Radioactive Waste, eds., G.S. Barney, J.D. Navratil, and W.W. Shulz, ACS Symposium Series 246, American Chemical Society, Washington, DC, 1984.

ADK (15)

ATTACHMENT 2

NRC DATA EXAMINATION FOR HYDRAZINE EXPERIMENTS

Date:	July 21-22, 1987
Location:	300 Area, 331 Building, Room 69 (3rd floor)
Parties:	NRC State of Washington State of Oregon Yakima Indian Nation Confederated Tribes of the Umatilla Indian Reservation Nez Perce Tribe

<u>July 21</u>

8:30 a.m.	Introductory comments by DOE and NRC
8:45	Meeting Protocol
9:00	Description of hydrazine experiment records
9:15	Data examination
3:15 p.m.	Return records to files
3:30	Clarification/questions/responses

<u>July 22</u>

8:30 a.m.	Continue data examination
1:00 p.m.	Clarification/questions/responses
3:15	Return records to files
3:20	Collection of "Request for Approval" forms
3:30	Summary and discussion as needed
4:30	End of data examination

<u>July 23</u> Additional time may be made available if requested by the NRC.

ADK ①

HEDEMP

ATTACHMENT 3

HYDRAZINE EXPERIMENTS DATA EXAMINATION MEETING PROTOCOL
JULY 21-22, 1987

- A conference room has been made available for the date examination. Attendees will log in. (Room 69, Bldg. 331)
- Attendees will be provided an index of records.
- Records will be requested through the Westinghouse Licensing representative. (F. Macdonald)
- All records will be returned to the files each day at 3:15 p.m.
- Workday extension will be considered if requested in advance (requires scheduling of technical and clerical staff and escorts).
- Files requested by the affected parties are working files and are not to be copied.
- Copies of data are available upon request through the Licensing Representative.
- Forms will be provided for submitting data clarification questions.
- Discussion will only involve clarification of the data records; data interpretation will not be part of the data examination.
- A close-out session with DOE management of the data examination will be at 3:30 p.m., July 22, as needed.
- Additional time may be made available on July 23, if this is requested by the NRC.

ADK (2)

ATTACHMENT 4

NRC DATA REQUEST FOR BASALT-SITE HYDRAZINE DATA REVIEW

NRC Concern 1 Exp. redox conditions not reflect site conditions

(1)

a. Notebook BNW 3535, page 27 — titration of redox buffers used in some tests

b. $AgCl + e^- \rightleftarrows Ag^+ + Cl^-$, reference electrode potential = 222 mV, Handbook of Chemistry and Physics, 1977, page D141. OK

(2), (3), (4)

a. Unreported ^{99}Tc and other radionuclide extraction data

b. Technetium-Iron Oxide Reactions Under Anaerobic Conditions: A Fourier Transform Infrared, FTIR Study. R. I. Haines, T. T. Vandergraaf and D. G. Owen, September 1986, AECL-9172.

c. Basalt-Radionuclide Sorption/Solubility Studies for the Engineered Barriers Department, Basalt Waste Isolation Project: FY 1986 Progress Report. L. L. Ames, J. E. McGarrah, B. A. Walker and T. L. Ehlert-Long, March 1986, pages 8-16, Figures 7, 8, 9.

d. October 1983 Monthly Report, page 2, Table 2

e. Status Report on the Evaluation of XPS and XRD Methods for Characterizing Sorbed and Precipitated Radionuclides. J. W. Shade and L. S. Dake, July 1986.

(5)

a. February 1983 Monthly Report, page 1, attached XRD data

b. Notebook BNW 3535, pages 68-72.

(6)

a. Radionuclide Solubility and Sorption Studies on Basalt FY 1983 Annual Report. L. L. Ames, J. E. McGarrah and B. A. Walker, November 1983.

b. BNW Notebooks Numbered 3535, 3636, 5019, 5020, 5423, 5424.

NRC Concern 2 hydrazine test pH not reflect site pH conditions

(7) We (PNL) did not readjust groundwater pH after addition of hydrazine.

NRC Concern 4 GEN. COMMENT LITTLE DIRECT COMPARISON

(8)

a. April 1982 Monthly Report, pages 3 and 4, Figure 4, 5, Table 3.

b. Notebooks BNW 5019, pages 80, 129, BNW 5020, pages 73, 88.

ADK 16

c. Notebook BNW pages 45-49.

d. Technetium and Actinide Sorption on Magnetite and Hematite. J. W. Shade, June 1986.

e. Letter Report L2D3P-86-2, October 21, 1985.

(9)

a. Solubility of Selected Radionuclides in the Basalt-Groundwater System at 60°C, Interim Report. L. L. Ames, J. E. McGarrah and B. A. Walker, May 1983, pages 50-65.

b. Notebook BNW 5424, pages 28, 29, 38, 39.

(10)

a. June 1982 Monthly Report, pages 1-3, Tables 1 through 8, Figures 1 through 3.

b. Notebook BNW 5019, pages 96-101.

c. November 1981 Monthly Report, pages 4-6, Tables 5 and 6.

d. Notebook BNW 5019, pages 21-25.

e. Selenate-Selenium Sorption On a Columbia River Basalt (Umtanum Basalt, Washington, U.S.A.). L. L. Ames, P. F. Salter, J. E. McGarrah and B. A. Walker, Chem. Geol., 43, pages 287-302 (1984).

f. Neptunium Adsorption on Synthetic Amorphous Iron Oxyhydroxide. D. C. Girvin, L. L. Ames, A. P. Schwab and J. E. McGarrah, December 1983.

g. August 1982 Monthly Report, pages 2, 3, 6, Tables 1, 5, 13, Figures 1, 3, 9.

h. September 1982 Monthly Report, pages 4 and 5, Tables 10, 13, Figures 5, 7.

i. July 1982 Monthly Report, pages 4 and 5, Tables 5, 11, 13, Figures 1, 2, 3, 7, 8.

j. Notebook 5019, pages 131, 137, 138, 124, 126, 128
Notebook 5020, pages 94, 90, 87, 85, 82.

(11), (16)

a. December 1981 Monthly Report, pages 3-5, Table 6.

<u>NRC Concern 6</u>

(12), (15)

a. October 1981 Monthly Report, page 1, Table 1.

b. January 1982 Monthly Report, page 7, Tables 13 and 14. - not relevant - studied org. c release into D.W.

(13) We (PNL) did not use polycarbonate tubes with hydrazine at 85°C. See McGarrah [1980 notebook] work at 23-65°C

(14) Experimental conditions (synthetic groundwater composition, temperature, geologic media) changed rapidly during the time hydrazine was used, effectively preventing the exact duplication of the polycarbonate container experiments in other containers.

(17) Scott Barney will furnish this information.

ADK (18)

INDEX FOR RADIONUCLIDE SORPTION WORK USING HYDRAZINE

G. S. BARNEY

Request for Supporting Data

1. Calculations used to obtain Eh values

   Theoretical calculations were based on standard potentials for the reactions:

   $N_2H_4 + 4OH^- = N_2 + 4H_2O + 4e^- \quad E^0 = +1.16$

   and

   $O_2 + 2H_2O + 4e^- = 4OH^- \quad E^0 = +0.401.$

   Assuming a pH of 9 and 0.8 atm of N_2 and 0.2 atm of O_2 gives calculated Eh values of -0.8 and +0.6 volts in the presence of 0.05 M hydrazine and in the presence of air, respectively.

2. Direct chemical analysis of reduced radionuclides

   Concentrations of radionuclides are generally too low to use so-called "direct chemical analysis" (spectrophotometry and electrochemistry). Indirect properties of oxidized and reduced species must be used such as (1) solvent extraction behavior or (2) sorption/desorption behavior.

   See RHO-N-458 p. 19, 43, 53, 57, 63, 69 *effects matrix - in polycarbonate*
   RHO-N-459 p. 3 *- groundwater composition effects*
   RHO-N-3 p. 145 *- sorp. kinetics - sec. min. + altered basalt*

   direct methods not used

3. Kinetics of hydrazine reactions with radionuclides

   See RHO-N-458 p. 13, 31, 39, 57, 63, 73, 77
   RHO-N-459 p. 3.
   RHO-N-3 p. 145

   SAME

   Identity of reaction products
   (See data for request #1)

4. Kinetics of hydrazine-radionuclide reactions and identity of reaction products
   (See data for requests 2 and 3)

5. Kinetics of hydrazine-selenate (selenite?) reaction and identity of reaction products *Se pptn. + sorption ± G.W. components*

   See RHO-N-458 p. 13, 31, 39, 53, 73 *- I.X. ident. used*

   G.W. rxns - relevant; selenite reducing agents - SX used

   RXN products not identified directly

6. Relative rates of hydrazine-radionuclide reactions and oxygen-radionuclide reactions

   No oxygen-radionuclide reaction rates were studied.

7. Use of acid to reestablish the pH of the groundwater

   See RHO-N-458 p. 11, 57, 63, 73, 77, 85 *ok*

   pH correct NaOH + HCl added

8. Comparisons of sorption of radionuclides reduced by hydrazine and by other means

   See RHO-N-458 p. 39, 53

   (selenite) Se by BH_4^-, $S_2O_4^{2-}$, $S_2O_5^-$; Selenite SO_3^{-2}, HS^-

   Comment only selenium

ADK (19)

9. Investigations that differentiate between ion-exchange and surface complexation mechanisms for sorption of radionuclides not reduced by hydrazine

See RHO-N-458 p. 85

not relevant — RHO-N-459 p. 3 — groundwater effects matrix test done in polycarbonate tubes.

10. Investigations that identify sorption mechanisms of "key" radionuclides

(See data for request #9)

11. Studies of interactions of hydrazine with minerals

See L. L. Ames data.

12. Studies of interactions of hydrazine with container materials

See L. L. Ames data.

13. Repeated sorption experiments at 85 °C with hydrazine-containing groundwaters in containers other than polycarbonate

See RHO-N-458 p. 57 - expts. with backfill in Teflon, not repeat of earlier work with sandstone in polycarbonate

14. Analysis of sorption data obtained using polycarbonate tubes to determine which data is invalid due to interactions with the tubes

No specific analysis could be found. However, essentially all the data that are used in transport calculations have been obtained or verified by recent measurements in which other container materials (glass or Teflon) have been used. Polycarbonate tubes have not been used since ~1981.

15. Resistance of attack of containers by hydrazine

(See data for rquest #12)

NOT RELEVANT

16. Studies of the stability of hydrazine over the times employed in sorption experiments

See RHO-N-458 p. 77 Study of Tc sorption on backfill with various N_2H_4 concs. N_2H_4 stability infered by pros. fabs. of sorption - no direct analysis

17. Laboratory procedures and records/data for tests that support (1) Figure 1 and Tables III and VII in Barney 1983, (2) Figure 1 and Tables III and VII in Barney 1984, (3) Figures 1 and 3, and Tables 2 and 7 in Barney 1982a, and (4) Figures 1 and 3, and Tables 2 and 7 presented in Barney 1982b

polycarbonate tubes - p. 4 hydrazine attack noted

(1) RHO-N-458 p. 3, RHO-N-459 p. 3

(2) same as above

(3) same as above

(4) same as above

factorial study polycarbonate tubes

done one time

general obs. '81 polycarbonate '82 polyethylene '83 Teflon

Sandstone tests in polycarbonate p. 3

Mustor interbed tests in polyethylene p. 13

Selenium tests + Mustor interbed in polyethylene

S. w. backfill Teflon

ADK (20)

ATTACHMENT 5

DATA CLARIFICATION QUESTIONS (1)

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

NAME OF REQUESTOR: Brooks

ORGANIZATION REPRESENTING: NRC

DATE/TIME: 07/22

QUESTION: Is the Salter and Jacobs sorption and solubility data package (SD-BWI-DP-001) still considered the operational data package for use in modeling calculations, or is there a later, post 1983, analysis and summary of radionuclide sorption data? This question is relevant to this N2H4 data review because Salter and Jacobs used, according to the description in their report, sorption values obtained (COVER)

DATE/TIME RESPONSE PROVIDED:

NAME OF RESPONDER:

in the presence of hydrazine. Because of the date of Salter and Jacobs, 1983, it seems possible that early RHO data obtained in polycarbonate tubes at elevated temps. could have been included in Salter and Jacobs. Based on more recent analyses, such data could be suspect due to hydrazine-polycarbonate reactions, hydrazine rock reactions etc. Therefore, the NRC is interested in understanding the current data base being used to supply radionuclide sorption data for site modeling activities.

DATA CLARIFICATION QUESTIONS

(2)

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

NAME OF REQUESTOR: Brooks

ORGANIZATION REPRESENTING: NRC

DATE/TIME: 21 July

QUESTION: On page 63 of BNW 3535 it is noted that based on the reported data pp 63 - 66, hydrazine - polycarbonate effects noted and "Data reported in Jan. 81 monthly." We would like to see the Jan. 81 monthly. It is not clear how these data show hydrazine - polycarbonate effects.

DATE/TIME RESPONSE PROVIDED:

NAME OF RESPONDER:

DATA CLARIFICATION QUESTIONS ③

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

NAME OF REQUESTOR: Brooks

ORGANIZATION REPRESENTING: NRC

DATE/TIME: 07/22 — Berry

QUESTION: NRC Concern 1, data/information need 1 addressed the various Eh values reported for "oxidizing" (+0.2, +0.5, +0.6 V) or "reducing" (-0.4 or -0.8 V) test conditions in various BWIP or PNL publications. The information identified for the data review did not show how the various values were calculated; especially why "oxidizing" values cover such a large range. Is there additional information supportive of the various publications?

this is the real range

DATE/TIME RESPONSE PROVIDED:

NAME OF RESPONDER:

DATA CLARIFICATION QUESTIONS ④

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

NAME OF REQUESTOR: Brooks

ORGANIZATION REPRESENTING: NRC

DATE/TIME: 07/22

not thought to be important

QUESTION: NRC Concern 4, data/information needs 8, 9, 10, 11, addresses the reactions which may occur between hydrazine and the sorbing substrate, rock, minerals, etc. Information published by other projects reports that hydrazine can adsorb or react with geologic materials. Such reactions might be expected to alter (increase or decrease) radionuclide sorption. In the data/information needs we were searching for either direct or

(OVER)

DATE/TIME RESPONSE PROVIDED:

NAME OF RESPONDER:

indirect evidence of such reactions in the PNL or RHO tests. In the information made available, we have not seen direct studies (SEM, XRD, physical properties) of sorption-test substrates before and after exposure to hydrazine-containing solutions.

The question: Does any other experimental information exist which could respond to this concern?

DATA CLARIFICATION QUESTIONS (5)

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

NAME OF REQUESTOR: Brooks

ORGANIZATION REPRESENTING: NRC

DATE/TIME: 07/22

QUESTION: NRC concern 6, data/information needs 12-17 deal with the reactions which may occur between hydrazine and various test container materials. Two potential problems could result from such reactions. One, degradation products resulting from attack on the plastic could interfere with or alter radionuclide sorption onto substrates. Second, much or all of the hydrazine could be consumed by reactions with the container and, thus, (OVER)

(based on evidence that hydrazine was not being sorbed)

DATE/TIME RESPONSE PROVIDED:

NAME OF RESPONDER:

little or no hydrazine would remain in solution to poise the system Eh. The information available during this data review does not contain evidence of a systemmatic evaluation of these questions. E.g., tests with distilled water and various plastic containers do not, obviously, shed light on possible hydrazine reactions.

The question: Is there any other data/information which addresses this NRC concern?

[redacted]

DATA CLARIFICATION QUESTIONS (6)

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

NAME OF REQUESTOR: Brooks

Gerber/sorption mechanism

ORGANIZATION REPRESENTING: NRC

DATE/TIME: 07/23

QUESTION: NRC concern 4, data/information need 10 was prompted by statements in the DOE response to the NRC draft STP (Ontiveros 1987) that key radionuclides are not sorbed by ion exchange mechanisms, and statements differentiating between ion exchange sorption and surface complexation sorption. Is was difficult for us to make the connection between this need #10 and the many references made available at the data review (COVER)

DATE/TIME RESPONSE PROVIDED: ______

NAME OF RESPONDER: ______

in responee to # 10. Is there additional information, summaries, discussions, etc. which would explain the difference between ion exchange and surface complexation reactions, and how the evidence presented supports the conclusions of Anttonen 1987 ?

DATA CLARIFICATION QUESTIONS ⑦

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

Cs solids

NAME OF REQUESTOR: D. Brooks

ORGANIZATION REPRESENTING: NRC

DATE/TIME: 07/22

QUESTION: What is the basis for the different approaches taken at PNL and RHO with the respect to the use of acid to readjust the solution pH after the addition of hydrazine.

in ph units 10 to 9.5 about .2 pH units

This question relates to NRC concern 2, data/information need 7. Our review of documents seemed to indicate that in RHO experiments acid was added to compensate for the OH^- associated with (over)

Also Scott

DATE/TIME RESPONSE PROVIDED:

NAME OF RESPONDER:

N_2H_4, while in PNL experiments the N_2H_4 was added last and the pH was not readjusted with acid. We are concerned that these different methodologies may make comparison of PNL/RHO data difficult, and that without addition of acid the solution pH would be more basic than expected in-situ. More basic pH could alter hydrolytic species of actinides, change groundwater/rock reactions, etc.

DATA CLARIFICATION QUESTIONS (8)

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

NAME OF REQUESTOR: Brooks

ORGANIZATION REPRESENTING: NRC

DATE/TIME: 07/22

QUESTION:

~~[illegible]~~ Fig 1 and Tabe III, in RHO-BW-SA-291 P present data for radionuclide sorption on ~~[illegible]~~ sandstone in presence of hydrazine for reducing conditions. The methods section of This report states tests were run in polyethylene tubes. The supporting documentation made available at The data review (RHO-N-458, p.3; RHO-N-459, p.3) state That tests were run in polycarbonate tubes. Question: Is There other data (COVER)

DATE/TIME RESPONSE PROVIDED:

NAME OF RESPONDER:

for tests in polyethylene tubes as described in RHO-BW-SA-291P ?

This question is related to NRC concern 6, data/information need 13 and 17.

DATA CLARIFICATION QUESTIONS (9)

FOR THE HYDRAZINE DATA EXAMINATION

JULY 21-22, 1987

NAME OF REQUESTOR: AD Kelmers

ORGANIZATION REPRESENTING: NRC

DATE/TIME: July 21

QUESTION:

Does footnote at bottom of p. 150 of notebook RHO-N-3 mean that N_2H_4 originally added had decomposed or been exhausted by 9/24/80 and additional N_2H_4 had to be added?

DATE/TIME RESPONSE PROVIDED:

NAME OF RESPONDER: