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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 uncertainties associated with the methods and strategies.

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].) 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

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

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

- <u>Kinetics of Rock-Groundwater Interactions</u>
  - 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

<u>3.1.3.5 Mineralogy</u>.

- <u>Thermodynamic stabilities and reaction kinetics of the minerals in Hanford Site rocks</u>
  - rock/water interactions test (see 3.1.3.4)
- <u>Chemical compositions of the minerals in Hanford Site rocks</u>
  - XRD, EMP, SEM, TEM, XRF, INAA, etc.
- <u>Solubilities of the minerals in Hanford Site rocks</u>
  - 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

3.2 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

3.3 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

3.4 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 preemplacement 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

3.5 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.

3.6 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 km^2 and extends horizontally no more than 5 km 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

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	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]From 40 CFR 191, Appendix A, Table 1.

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

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 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 with groundwater. 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 an 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

3.7 UNCERTAINTY ASSOCIATED WITH THE METHODS AND STRATEGIES FOR OBTAINING THE DATA AND INFORMATION NEEDS

There are many difficulties in attempting to establish "acceptable" or even "attainable" uncertainties for all the parameters needed for the successful completion of any engineering project. However, when one component of the project involves a natural geologic environment, as in the case of a high-level nuclear waste repository, the difficulties are compounded manyfold. Uncertainties have their source not only in the natural variability encountered on even the smallest scale within a single geologic system, but also in the methods available to analyze the parameters of interest as well. For example, one would use significantly different methods to determine the mineralogic composition of a well-crystallized rock versus a poorly-crystallized one. In addition to the difference in uncertainty as a result of the differing heterogeneity of the samples, the two methods used would have different inherent uncertainties that might not be comparable in magnitude. Similarly, the measurement of pH in brine solutions, as compared with pH measurement in solutions of low ionic strength, involves a whole new set of problems and an unavoidable increase in uncertainty as a result of electrode instability and high ionic-strength complications. Thus, in attempting to assign acceptable levels of uncertainty, each measurement must be evaluated for its ultimate purpose and use, as well as whether these levels of uncertainty may be attainable using standard practices or if they would require the development of new techniques.

The acceptable, or even the attainable, uncertainty for a given parameter is not an absolute number, but rather a context-sensitive parameter. It is not possible at this time to define the desired level of uncertainty for each parameter discussed in sections 3.1 through 3.6. Information on the manner in which DOE will use the data is required. The ultimate use of the data should be defined on a case-specific basis prior to the collection of the data so that the needed precision and accuracy can be determined. If possible, sensitivity analyses should be performed to assist in establishing the level of precision and accuracy needed to address the issue of interest. For example, one could go through extraordinary efforts to reduce the uncertainty of some parameter; however, if the parameter itself is not critical to the final result or if uncertainties in other parameters dominate the application or use of the parameter, then uncertainties resulting from standard laboratory practices may be acceptable and the extraordinary effort unnecessary. In general, it is desirable to achieve the best uncertainty possible without resorting to extraordinary measures.

In assessing uncertainties for various parameters, one must keep in mind the anticipated use of the data as well as what uncertainties are attainable using standard practices. Consideration of: (1) the sensitivity of final results to the parameters being measured, (2) the methods available for use, and (3) the natural variability in geologic systems that one has no control over will help to guide the establishment of uncertainty limits for repository systems.

The following sections do not address the uncertainty associated with specific parameters and methods presented in sections 3.1 through 3.6. Instead, examples are given using key parameters to illustrate how the context in which the data will be used governs the desirable level of uncertainty to be attained.

3.7.1. Temperature

Temperature can be measured with a precision/accuracy of fractions of a degree if desired. In a repository setting, temperature will affect mineral solubilities and decomposition, solution speciation, thermodynamic calculations, waste package corrosion characteristics, etc. None of these parameters are sensitive on the scale of fractions of a degree, but more on the scale of 10's of degrees. An exception would be around the freezing and boiling point of water where a difference of a few degrees would make a large difference in the volume and thermodynamic properties of the fluid (liquid to solid, or liquid to gas). Hence, although temperature can be measured with a small uncertainty, the extraordinary effort to measure it to fractions of a degree is unnecessary and the usual precision of a few degrees (e.g, <10°C) is adequate for resolving the issues of concern, even close to the boiling and freezing points of water.

3.7.2. Pressure

Pressure, similar to temperature, can be measured with great precision and accuracy but most of the parameters of concern in a repository setting (as given under temperature) are quite insensitive to even relatively large changes in pressure - on the order of tens of bars. Thus, extraordinary methods for determining pressure are unnecessary.

3.7.3. Aqueous chemical composition

The uncertainty of the aqueous chemical composition will vary greatly as a function of the species of interest, the absolute concentration of that species, and the concentration of the other species present, commonly known as the matrix. Detection limits and precision will vary from one technique to another (e.g., AA, ICP, IC), as well as with the care taken during sample preparation. Since electroneutrality must be maintained in a solution, an estimate of the net uncertainty of a solution analysis can be obtained from the charge balance and the difference between the positive and negative charges should, in general, be less than 10%. While this parameter does provide an estimate of the uncertainty for the major chemical species it does not do so for the minor and trace species, which do not significantly contribute to the charge balance of a solution. In addition, even though a species may be a minor or trace component, a smaller uncertainty for this parameter may be more important then that for a major element. For example, although sodium is often a major species it is relatively inert, participating in few precipitation or complexation reactions. In contrast, iron, which is a species often present in much lower abundance, can be an excellent scavenger of radionuclides when it precipitates in either an oxic or reduced form. Hence, a lower detection limit and better precision may be required for iron than for sodium, even though its absolute abundance is much lower than sodium.

The pH of groundwaters is often a critical parameter in controlling radionuclide migration, yet the uncertainty required for it is also context sensitive. For example, if the pH is near the absorption edge for a key radionuclide, or if the pH is close to the protonation or deprotonation of an important species (e.g. $H_2CO_3/HCO_3^-/CO_3^{2-}$, NH_3/NH_4^+, CH_3COOH/CH_3COO^-, H_2S/HS^-), for its intrinsic interest or for its buffering capacity, then small changes in the pH and accompanying uncertainties are important. Alternatively, if the pH is far from such a value it is less important and higher uncertainties are acceptable.

3.7.4. Redox state

The redox state of a water-solid system will determine the oxidation state of the dissolved species and thus affect complexation and transport as well as precipitation and dissolution reactions. In most natural waters different redox couples (e.g. Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{4+}, S^{2-}/SO_4^{2-}, $NH_4^+/NO_2^-/NO_3^-$) give different redox states and a "system" redox cannot be uniquely defined in most cases. The redox state of a system is important to the extent of whether a given scavenging phase such as FeOOH, MnO_2 or FeS_x will precipitate or dissolve, but as long the system is within the stability fields of these minerals it may be less important to know "how oxic" or "how reducing" the system is. The redox would also be critical with respect to the oxidation state of certain radionuclides, but away from the critical zones where aqueous species of these elements change or where radionuclide-bearing minerals precipitate it is less important. Thus, near selected redox boundaries, which will be system dependent, the redox state must be known with lesser uncertainties than in other ranges away from these boundaries.

3.7.5. Mineralogy

Determining the mineralogic composition of rocks by x-ray diffraction techniques ranges from an almost purely qualitative to quantitative procedure, and will be highly dependent on the methods used. While qualitative or even semiquantitative x-ray diffraction techniques are fairly standard for most rocks and minerals, to achieve good quantitation, or the quantitation of unusual or poorly crystallized materials, can require vast amounts of additional work. The acceptable uncertainty in the determination of the mineralogy (wt %) of rocks from repository settings will depend on the context as well as the specific mineralogy. For example, knowing the percentage of quartz, which is a relatively inert phase except for providing a source of silica to the system, will be less important than knowing the percentage of zeolite, even if the quartz is present in much greater abundance. Also the important minerals will change from site to site. For example, the presence, absence and abundance of zeolites will be important at Hanford and Yucca Mt. while the clays will be equally important at Deaf Smith.

3.7.6. Bulk Composition of the Solid Phase

It is likely that certain components in the bulk composition of phases present in candidate rocks will be critical to the performance of the repository, while others will play a relatively minor role. The methods are well established for determining the major element composition with relatively low uncertainty (e.g., electron microprobe - ±2-5 wt %), although proper standardization is often the key to this result and may not be trivial in itself. Quantitation of trace components is more difficult and the uncertainty with which their concentrations need to be determined will vary on an element-by-element basis as well as on a case-specific basis. For example, the quantity of reduced iron may be more critical to the Hanford system than for the Yucca Mt. system because of the emphasis on redox state in the basalts at Hanford.

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LETTER REPORT

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

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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 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 uncertainties associated with the methods and strategies.

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 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 (i.e., non-potable water) 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

3.2 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 design for waste packages in the proposed Yucca Mountain repository 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

3.3 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 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 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

3.4 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

3.5 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.

3.6 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 perfor-mance 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 km^2 and extends horizontally no more than 5 km 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, Table 1.
[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(l)].) Thus, the EPA term "disposal" is equivalent to the NRC term "permanent closure". A number of extended footnotes to Table 1 of Appendix A, Part 191, define units of waste and explain the application of the release limits to different types of waste. 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 multistage 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.

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

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, lazer-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.

3.7 UNCERTAINTY ASSOCIATED WITH THE METHODS AND STRATEGIES FOR OBTAINING THE DATA AND INFORMATION NEEDS

There are many difficulties in attempting to establish "acceptable" or even "attainable" uncertainties for all the parameters needed for the successful completion of any engineering project. However, when one component of the project involves a natural geologic environment, as in the case of a high-level nuclear waste repository, the difficulties are compounded manyfold. Uncertainties have their source not only in the natural variability encountered on even the smallest scale within a single geologic system, but also in the methods available to analyze the parameters of interest as well. For example, one would use significantly different methods to determine the mineralogic composition of a well-crystallized rock versus a poorly-crystallized one. In addition to the difference in uncertainty as a result of the differing heterogeneity of the samples, the two methods used would have different inherent uncertainties that might not be comparable in magnitude. Similarly, the measurement of pH in brine solutions, as compared with pH measurement in solutions of low ionic strength, involves a whole new set of problems and an unavoidable increase in uncertainty as a result of electrode instability and high ionic-strength complications. Thus, in attempting to assign acceptable levels of uncertainty, each measurement must be evaluated for its ultimate purpose and use, as well as whether these levels of uncertainty may be attainable using standard practices or if they would require the development of new techniques.

The acceptable, or even the attainable, uncertainty for a given parameter is not an absolute number, but rather a context-sensitive parameter. It is not possible at this time to define the desired level of uncertainty for each parameter discussed in sections 3.1 through 3.6. Information on the manner in which DOE will use the data is required. The ultimate use of the data should be defined on a case-specific basis prior to the collection of the data so that the needed precision and accuracy can be determined. If possible, sensitivity analyses should be performed to assist in establishing the level of precision and accuracy needed to address the issue of interest. For example, one could go through extraordinary efforts to reduce the uncertainty of some parameter; however, if the parameter itself is not critical to the final result or if uncertainties in other parameters dominate the application or use of the parameter, then uncertainties resulting from standard laboratory practices may be acceptable and the extraordinary effort unnecessary. In general, it is desirable to achieve the best uncertainty possible without resorting to extraordinary measures.

In assessing uncertainties for various parameters, one must keep in mind the anticipated use of the data as well as what uncertainties are attainable using standard practices. Consideration of: (1) the sensitivity of final results to the parameters being measured, (2) the methods available for use, and (3) the natural variability in geologic systems that one has no control over will help to guide the establishment of uncertainty limits for repository systems.

The following sections do not address the uncertainty associated with specific parameters and methods presented in sections 3.1 through 3.6. Instead, examples are given using key parameters to illustrate how the context in which the data will be used governs the desirable level of uncertainty to be attained.

3.7.1. Temperature

Temperature can be measured with a precision/accuracy of fractions of a degree if desired. In a repository setting, temperature will affect mineral solubilities and decomposition, solution speciation, thermodynamic calculations, waste package corrosion characteristics, etc. None of these parameters are sensitive on the scale of fractions of a degree, but more on the scale of 10's of degrees. An exception would be around the freezing and boiling point of water where a difference of a few degrees would make a large difference in the volume and thermodynamic properties of the fluid (liquid to solid, or liquid to gas). Hence, although temperature can be measured with a small uncertainty, the extraordinary effort to measure it to fractions of a degree is unnecessary and the usual precision of a few degrees (e.g, <10°C) is adequate for resolving the issues of concern, even close to the boiling and freezing points of water.

3.7.2. Pressure

Pressure, similar to temperature, can be measured with great precision and accuracy but most of the parameters of concern in a repository setting (as given under temperature) are quite insensitive to even relatively large changes in pressure - on the order of tens of bars. Thus, extraordinary methods for determining pressure are unnecessary.

3.7.3. Aqueous chemical composition

The uncertainty of the aqueous chemical composition will vary greatly as a function of the species of interest, the absolute concentration of that species, and the concentration of the other species present, commonly known as the matrix. Detection limits and precision will vary from one technique to another (e.g., AA, ICP, IC), as well as with the care taken during sample preparation. Since electroneutrality must be maintained in a solution, an estimate of the net uncertainty of a solution analysis can be obtained from the charge balance and the difference between the positive and negative charges should, in general, be less than 10%. While this parameter does provide an estimate of the uncertainty for the major chemical species it does not do so for the minor and trace species, which do not significantly contribute to the charge balance of a solution. In addition, even though a species may be a minor or trace component, a smaller uncertainty for this parameter may be more important then that for a major element. For example, although sodium is often a major species it is relatively inert, participating in few precipitation or complexation reactions. In contrast, iron, which is a species often present in much lower abundance, can be an excellent scavenger of radionuclides when it precipitates in either an oxic or reduced form. Hence, a lower detection limit and better precision may be required for iron than for sodium, even though its absolute abundance is much lower than sodium.

The pH of groundwaters is often a critical parameter in controlling radionuclide migration, yet the uncertainty required for it is also context sensitive. For example, if the pH is near the absorption edge for a key radionuclide, or if the pH is close to the protonation or deprotonation of an important species (e.g. $H_2CO_3/HCO_3^-/CO_3^{2-}$, NH_3/NH_4^+, CH_3COOH/CH_3COO^-, H_2S/HS^-), for its intrinsic interest or for its buffering capacity, then small changes in the pH and accompanying uncertainties are important. Alternatively, if the pH is far from such a value it is less important and higher uncertainties are acceptable.

3.7.4. Redox state

The redox state of a water-solid system will determine the oxidation state of the dissolved species and thus affect complexation and transport as well as precipitation and dissolution reactions. In most natural waters different redox couples (e.g. Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{4+}, S^{2-}/SO_4^{2-}, $NH_4^+/NO_2^-/NO_3^-$) give different redox states and a "system" redox cannot be uniquely defined in most cases. The redox state of a system is important to the extent of whether a given scavenging phase such as FeOOH, MnO_2 or FeS_x will precipitate or dissolve, but as long the system is within the stability fields of these minerals it may be less important to know "how oxic" or "how reducing" the system is. The redox would also be critical with respect to the oxidation state of certain radionuclides, but away from the critical zones where aqueous species of these elements change or where radionuclide-bearing minerals precipitate it is less important. Thus, near selected redox boundaries, which will be system dependent, the redox state must be known with lesser uncertainties than in other ranges away from these boundaries.

3.7.5. Mineralogy

Determining the mineralogic composition of rocks by x-ray diffraction techniques ranges from an almost purely qualitative to quantitative procedure, and will be highly dependent on the methods used. While qualitative or even semiquantitative x-ray diffraction techniques are fairly standard for most rocks and minerals, to achieve good quantitation, or the quantitation of unusual or poorly crystallized materials, can require vast amounts of additional work. The acceptable uncertainty in the determination of the mineralogy (wt %) of rocks from repository settings will depend on the context as well as the specific mineralogy. For example, knowing the percentage of quartz, which is a relatively inert phase except for providing a source of silica to the system, will be less important than knowing the percentage of zeolite, even if the quartz is present in much greater abundance. Also the important minerals will change from site to site. For example, the presence, absence and abundance of zeolites will be important at Hanford and Yucca Mt. while the clays will be equally important at Deaf Smith.

3.7.6. Bulk Composition of the Solid Phase

It is likely that certain components in the bulk composition of phases present in candidate rocks will be critical to the performance of the repository, while others will play a relatively minor role. The methods are well established for determining the major element composition with relatively low uncertainty (e.g., electron microprobe - ±2-5 wt %), although proper standardization is often the key to this result and may not be trivial in itself. Quantitation of trace components is more difficult and the uncertainty with which their concentrations need to be determined will vary on an element-by-element basis as well as on a case-specific basis. For example, the quantity of reduced iron may be more critical to the Hanford system than for the Yucca Mt. system because of the emphasis on redox state in the basalts at Hanford.

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