

ADK Comments 08/08/84

MAJOR COMMENT - The amount of work required to quantify all the reactions/processes/conditions identified in Section 3.3 may be much greater than the time and \$'s available. I suggest revision of the approach to include the concepts of emphasis of key radionuclides and use or measurement, of limiting conditions and bounding values for many reactions/processes/conditions.

SITE TECHNICAL POSITION - GEOCHEMISTRY
ISSUES FOR THE BASALT WASTE
ISOLATION PROJECT (BWIP)

conditions.

SECOND MAJOR COMMENT - In rereading Section 3.3, I found it very difficult to find much information that could be considered guidance for BWIP. The various issues are phrased as rhetorical questions which have then answered in the subsequent paragraph. I don't understand this approach to writing. It is possible that this portion of this draft document could profit from rethinking and revision. I agree.

- 1 S. TP
- 2 ICS - 2
- 3 JS -
- 4 IS -
- 5 SOW
- 6 E.A. vari
- 7 Gas cond.

JGB Comments 8/9/84

ADK Comments 8/9/84

Dave -
note comments
Walt

Issues for all sites (S&P, etc.) should be worked similarly, as they are applicable -- minor wording differences among the 3 STP's are confusing & misleading. ~~First possible~~

The discussion in this STP doesn't seem specific to BWIP, but rather generic. Is it possible to have a single STP or issues for all sites -- with appendices to account for site-specific differences? 1

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1.0 BACKGROUND

In the review of an application for Construction Authorization for a HLW geologic repository, the NRC is required to determine whether the site and design meet the Technical Criteria of 10 CFR Part 60 (Subpart E). The NRC staff determination will be based on the answers to, and supporting analyses of, technical questions concerning groundwater flow, geochemical retardation, waste form and package performance, geologic stability, and facility design. During the process of site characterization, the DOE will perform the laboratory and field investigations, ^{necessary} to develop the information needed to address these basic technical questions.

The investigations needed to characterize a geologic repository are complex and require long lead times. The Nuclear Waste Policy Act of 1982 (NWPA) has established a schedule for site characterization and selection. Specifically, NWPA requires publication of Site Characterization Plans (SCP's) by the DOE at an early stage of the process. Subsequent to receipt of an SCP the NRC must prepare a formal Site Characterization Analysis (SCA) for each site. NRC single-issue technical position papers, documented site reviews, and interagency technical meetings will precede and supplement the SCA's. Because of the complexity and long lead times for site characterization investigations, it is essential that activities be organized to make possible an NRC determination of site acceptability. Proper organization necessitates early identification of technical questions (specific issues) relevant to the specific site. Therefore, this document establishes the NRC position as to the essential technical questions relevant to the geochemistry of a repository in basalt at the Basalt Waste Isolation Project (BWIP). Other Site Technical Positions will address both NRC staff concerns regarding selected specific issues and acceptable technical approaches for addressing those specific issues. *

In identifying these essential issues, the staff has used a performance analysis approach. In that approach, three terms, site issues, performance issue and significant conditions and processes, have their special meanings described in the paragraphs below.

A Site Issue is a question about a specific site that must be addressed and resolved to complete the licensing assessment of site suitability and/or design suitability in terms of 10 CFR 60. Site issues are not necessarily controversial questions.

A Performance Issue is a broad question concerning the operation and long-term performance of the various components of the repository system. A set of performance issues are derived directly from the performance objectives in 10 CFR 60.

Significant Conditions and Processes, including potential adverse conditions of 10 CFR 60 (See Appendix A), are those that must be considered in the assessment of a performance issue and either (1) exist before repository disturbance, (2) could cause future changes, or (3) result from change. They may be natural (e.g., faulting), repository-included (e.g., thermal buoyancy), and human-induced (e.g., withdrawal of water resources). *derived?* *induced?* * *

In its performance analysis approach, the NRC staff first breaks down the performance objectives of 10 CFR 60 into a set of performance issues corresponding to the individual performance of the various components of the repository system. As developed in NUREG-0960, performance issues for a geologic repository are:

1. How do the design criteria and conceptual design address releases of radioactive materials to unrestricted areas within the limits specified in 10 CFR 60? *
2. How do the design criteria and conceptual design accommodate the retrievability option?
3. When and how does water contact the backfill?
4. When and how does water contact the waste package?
5. When and how does water contact the waste form?

} how much?
what rate?

6. When, how, and at what rate are radionuclides released from the waste form?
7. When, how, and at what rate are radionuclides released from the waste package?
8. When, how, and at what rate are radionuclides released from the backfill?
9. When, how, and at what rate are radionuclides released from the disturbed zone?
10. When, how, and at what rate are radionuclides released from the far field to the accessible environment?
11. What is the pre-waste emplacement groundwater travel time along the fastest path of radionuclide travel from the disturbed zone to the accessible environment?
12. Have the NEPA Environmental/Institutional/Siting requirements for nuclear facilities been met?

The next step in the performance analysis approach is identification of the significant conditions and processes that bear on assessment of each of the performance issues. Judgment is involved in determining which conditions and processes are considered significant. Knowledge gained from the staff's review of various related technical data and documents, site visits, technical meetings and research efforts contributed heavily to the particular selection of significant conditions and used in developing of this STP. Questions about the significant conditions and processes as they pertain to site geochemistry constitute the site issues identified in this position.

~ =
Rerwording
required.

Because the geochemistry of ^{the Hanford} BWIP Site will significantly affect repository performance, information on geochemistry during site characterization will be part of the total repository system information needs of the NRC staff required

*

1. INSERT "A"

* Issues STPs have been developed in five technical areas (1.0 GROUNDWATER; 2.0 WASTE FORM / WASTE PACKAGE; 3.0 GEOCHEMISTRY; 4.0 REPOSITORY DESIGN; and 5.0 GEOLOGY). The site issues developed in each STP are designated and numbered in accordance with the above numbering system. The sequential order in which technical areas have been numbered should not be interpreted as the order of relative importance.

of 10CFR60

to assess the performance elements (See Appendix B). Issues identified in the following section delineate information on geochemistry issues ^{at the Hanford Site} ~~at the BWIP site~~ needed by the NRC staff to assess adequately the performance issues. ~~Issues related to groundwater, waste form/waste package, repository design and geology are presented in other STPs.~~ The sequential order in which issues are identified should not be interpreted as the order of relative importance.

~ = wording could be improved.

2.0 TECHNICAL POSITION

It is the position of the NRC staff that, based on our current level of knowledge of the Basalt Waste Isolation Project (BWIP) investigations, assessments of the Technical Criteria (Subpart E) in 10 CFR Part 60 requires that, at a minimum, the following issues (and associated sub-issues) concerning site geochemistry be addressed.

3.0 GEOCHEMISTRY ISSUES*

ISSUE 3.1) WHAT ARE THE SITE GEOCHEMICAL CONDITIONS PRECEDING REPOSITORY DISTURBANCE AND WASTE EMPLACEMENT?

3.1.1 What is the mineralogy/petrology/chemistry of the disturbed zone and far field natural rock environment (host rock/interbed material) prior to repository disturbance and waste emplacement? ^{geochemistry?} *

3.1.1.1 What is the mineralogy/petrology/chemistry of secondary minerals of the disturbed zone and far field natural rock environment (host rock/interbed materials) prior to repository disturbance and waste emplacement? ^{aren't secondary minerals part of the natural environment?} *

3.1.2 What are the geochemical conditions of the groundwater in the disturbed zone and far field prior to repository disturbance and waste emplacement?

3.1.3 What is the mineralogy/petrology/chemistry of the backfill/packing/seals prior to repository disturbance and waste emplacement? ^{these are not core products of repository waste emplacement}

ISSUE 3.2) WHAT ARE THE CHANGES IN SITE GEOCHEMICAL CONDITIONS FOLLOWING REPOSITORY [DISTURBANCE] AND WASTE EMPLACEMENT CONSTRUCTION

* ADD "A" ^{better word?}

3.2.1 What are the changes in the mineralogy/petrology/chemistry of the natural rock environment (host rock/interbed material) under anticipated and unanticipated repository scenarios in the disturbed zone and in the far field, through time? *geochemistry?* *

3.2.1.1 What are the changes in the mineralogy/petrology/chemistry of secondary minerals associated with the natural rock environment under anticipated and unanticipated scenarios in the disturbed zone and far-field host rock, through time? *geochemistry?* *

3.2.2 What are the changes in the geochemical conditions of the groundwater under anticipated and unanticipated repository scenarios in the disturbed zone and in the far field, through time? *should we list what these are? pH, Eh, composition, colloids, etc., T and P*

3.2.3 What are the changes in the mineralogy/petrology/chemistry of back-fill/packing/seals under anticipated and unanticipated repository scenarios in the disturbed zone and in the far field, through time? *geochemistry?* * *are these in the far field?*

ISSUE 3.3 **WHAT ARE THE ANTICIPATED GEOCHEMICAL REACTIONS/PROCESSES/CONDITIONS AFFECTING RELEASE AND TRANSPORT OF RADIONUCLIDES TO THE ACCESSIBLE ENVIRONMENT?**

3.3.1 What is the expected solubility of released radionuclides in the disturbed zone and the far field through time? *apparent concentration limit?* *why not address "source term" instead?*

3.3.1.1 How does precipitation/co-precipitation affect radionuclide solubility/concentration?

3.3.1.2 How does speciation affect radionuclide solubility/concentration?

3.3.1.3 How do colloids affect radionuclide solubility/concentration?

3.3.1.4 How do organics affect radionuclide solubility/concentration?

It may prove extremely difficult to quantify some of these effects. Is it really necessary to explore each of these for each radionuclide?

categorization of sub-issues needs rethinking.

Next page

3.3.2 How do ~~chemical~~ changes in the mineralogy/petrology/chemistry of packing material/backfill/seals influence radionuclide migration/retardation through time? *

3.3.3 How will reaction and sorption kinetics affect radionuclide release and transport?

3.3.4 How do redox conditions affect radionuclide mobility? *Isn't this part of 3.3.1 and 3.3.2?*

~~3.4.1~~ What are the effects of gamma and alpha radiolysis on redox conditions? *Radiolysis product effects is a*

broad issue and should not be confined to redox conditions.

3.3.5 How does diffusion affect radionuclide migration/retardation in the near-field, and the far-field through time? *why near-field instead of disturbed zone?*

3.3.6 How do colloids/particulates affect radionuclide migration/retardation in the near-field and the far-field through time?

3.3.7 How do organics affect radionuclide migration/retardation in the near-field and the far-field through time?

3.0 DISCUSSION

Issue 1 covers the initial geochemical environment of the repository, ^{is} the geochemical baseline for the repository. Issue 2 covers changes to the initial geochemical environment, which will be ^{result from} ~~changed by~~ the mining and waste emplacement, and then changed further during heating ^{and radiolysis} due to decaying waste. Issue 3 deals with waste package/geological environment interactions and the ^{transport} of waste radionuclides to the accessible environment. The rationale for each geochemistry issue is described in the subsequent discussion. In the discussion, the broadest issues _x are those that would appear in the first tier of a hierarchy of issues and sub-issues, are related directly to the performance issues that are listed in the Background Section above. Sub-issues are related by technical argument to the broad issue(s). *

happen? DISAGREE! I agree!!

ISSUE 3.1 WHAT ARE THE SITE GEOCHEMICAL CONDITIONS PRECEDING REPOSITORY DISTURBANCE AND WASTE EMPLACEMENT?

An understanding of the geochemical conditions preceding ^{repository construction} [mining] and waste emplacement is necessary ^{support evaluation of} in order to ^{baseline information for predicting} [evaluate] the release of radionuclides from the disturbed zone to the accessible environment. Adverse conditions within the far-field are likely to remain unchanged after waste emplacement, whereas favorable prewaste emplacement conditions in the disturbed zone may alter to potentially adverse conditions. For these reasons, an understanding of the geochemical conditions prior to waste emplacement is necessary to establish a baseline for prediction of geochemical conditions under typical repository scenarios. These ^e ~~baseline~~ conditions are ^{needed} to evaluate Performance Issues 3, 7, 8, 9, and 10.

= whoops, you read my mind!

3.1.1 What is the mineralogy/petrology/chemistry of the disturbed zone and far field natural rock environment host rock/interbed material prior to repository disturbance and to waste emplacement?

Verbose.

The host rock is ^{one of} the primary barriers in geologic waste isolation. Knowledge of the mineralogy, petrology, and chemical composition will ^{help} lead to the necessary understanding of the genesis and future geochemical stability of the host rock, aid in the evaluation of the effects of waste/rock ^{interactions}, and provide information for interpreting groundwater chemistry.

Somewhat redundant.

3.1.1.1 What is the mineralogy/petrology/chemistry of secondary minerals in the disturbed zone and far field natural rock environment host rock/interbed material prior to repository disturbance and waste emplacement?

The Grande Ronde basalts have a fractured/jointed structure interspersed with vugs and possess relatively porous flow tops/bottoms. These host rock openings are generally filled with ^{w/c} secondary minerals that ^{are} derived mostly from the alteration of basalt by circulating ground water. These

Aren't joints fractures?



Is "diagenesis" an appropriate word to use describing alteration (formation of secondary minerals) in volcanic rocks?

potential
joints, fractures, and vesicular flow regions are pathways for groundwater ^{migration of} carrying radionuclides leached from the waste. the secondary minerals are expected to be a primary sorption medium in the retardation of radionuclides. Thus, understanding the diagenesis of alteration and secondary minerals will aid in interpreting the (1) groundwater chemistry and defining the retardation properties of the host rock prior to waste emplacement, and (2) as a baseline for predicting any alteration that may occur as the result of waste emplacement. An understanding of the existing distribution of alteration products may indicate potential release pathways of radionuclides. *Somewhat redundant.*

←
"understanding" a limiting concentration
* may not produce a limiting concentration

3.1.2 What are the geochemical conditions of the groundwater in the disturbed zone and the far field prior to repository disturbance and waste emplacement? *construction?*

groundwater is not site factor -- esp. if kinetic inhibitions are important.

* cations → Groundwater geochemical conditions, in particular temperature, pressure, pH, redox conditions, ionic strength, and presence of complexing ligands, determine which chemical species of radionuclides are most likely to form and determine what reactions are likely to occur. Reactions of radionuclides in solution with ^{phases} components of the backfill, the near field and far field host rock, including adsorption and precipitation, will determine the limiting concentrations of soluble species. *Knowledge of* Present conditions will be necessary for determining conditions in the far field, and will serve as a baseline for predicting changes resulting from increased temperature and pressure in the disturbed zone. *This is confusing -- adsorption*

* adsorption
* limiting concentration

3.1.3 What is the mineralogy/petrology/chemistry of the backfill/packing/seals prior to repository disturbance and waste emplacement? *geochemistry?* *consistent?*

Backfilling/packing/seals, as discussed here, refers to materials used to fill drillholes, emplacement holes, shafts, tunnels, and disposal rooms. The large man-made cavities and holes, including

←

Accessible environment?

fracturing around these cavities or holes, represent a broad and potentially short pathway to the biosphere for the radionuclides released from waste packages. The pathways must be blocked with engineered barriers that provide a means of geochemical retardation of radionuclide migration to eliminate the short circuit to the biosphere.

ISSUE 1.2 WHAT ARE THE CHANGES IN SITE GEOCHEMICAL CONDITIONS FOLLOWING REPOSITORY DISTURBANCE AND WASTE EMPLACEMENT?

The geochemical conditions/properties of the host rock surrounding the repository will be affected by construction and the emplacement of nuclear waste. Construction and increased temperatures in the vicinity of the repository may alter the properties of the basalt/secondary mineralogy to the extent that water is more/less accessible to the waste package and backfill (performance issues 3,4), affecting the release and transport of radionuclides to the accessible environment (performance issues 8,9,10).

You mean engineered facility, don't you?

Vague and therefore confusing

geochemistry?

3.2.1 What are the changes in the mineralogy/petrology/chemistry of the natural rock environment (host rock/interbed material) under anticipated and unanticipated repository scenarios in the disturbed zone and far field, through time.

stability not a word, a phrase/concept

Rock and mineral stabilities will be affected by repository construction and changes induced by waste emplacement. Many minerals exist in metastable states and the changes in temperature, pressure, and/or degree of saturation may alter the stability of the minerals in a rock. Stability changes will influence the sorptive properties of the host rock, and its ability to prevent water ingress on egression.

Including secondary minerals!

~ = ?

geochemistry?

Combine 3.2.1 and 3.2.1.1?

3.2.1.1 What are the changes in the mineralogy/petrology/chemistry of secondary minerals associated with natural rock environment under anticipated and unanticipated scenarios in the disturbed zone and far-field host rock, through time.

Why aren't secondary minerals part of the "natural rock environment"?

The secondary mineralogy associated with basalt is cited as a favorable condition for the retardation of radionuclides due to the sorptive capacity of zeolites and clays. Many minerals exist in metastable states and the change^s of temperature and/or pressure may alter the stability of the minerals in a rock. The alteration products, although often pseudomorphic after the original minerals, generally have different physical/chemical properties which ^{may} affect the initial retardation capacity of the host rock. The effects will depend on the amount of water present, and may vary significantly depending on the amount of water present. *Verbose sentence.*

3.2.2 What are the changes in the geochemical conditions of the groundwater under anticipated and unanticipated scenarios in the disturbed zone and far field, through time.

don't forget radiolysis which may generate stable organics from the Geochemical conditions, in particular temperature, pressure, pH, ^{CH₄ in BWIP} redox conditions, ionic strength, and presence of complexing ligands, ^{groundwater} determine which chemical species of radionuclides are most likely to form and determine what reactions are likely to occur. Reactions of radionuclides in solution with the existing ^{delete this word?} components of the backfill, ^{*} and the near-field and far-field host rock, will determine the limiting concentrations of soluble species. Changes in temperature and pressure alter the geochemical conditions of the groundwater which determine the mineral stabilities and may affect radionuclide migration. An assessment of the prevailing geochemical conditions associated with groundwater, in particular temperature, pH, redox conditions, ionic strength, and aqueous speciation, will be affected by repository-induced changes. These altered conditions will influence waste package and host rock stability and the ability of released radionuclides to migrate. (In addition, repository construction may cause new groundwater pathways to be formed.) *not a geochem. issue*

3.2.3 What are the changes in the mineralogy/petrology/chemistry of backfill/packing/seals under anticipated and unanticipated repository scenarios in the disturbed zone, through time?

don't forget gases, cations, colloids, etc.

not a clearly worded -

redundant? yes

eventually
- also decreases

As the temperature of the backfill and near-field/far-field host-rock increases with the time, minerals and ionic solubilities will change in an attempt to reequilibrate with the new conditions. Minerals may dissolve or precipitate, thereby altering the mineral distribution. The resultant change will depend on temperature, groundwater conditions and fluid flow regime (i.e., diffusion/convection or fracture flow). Precipitation of minerals may in turn alter the fluid flow path, and ultimately the migration of radionuclides. Thus, backfill/packing/seals will be affected by geochemical changes induced by waste emplacement, such as changes in temperature, pressure, and degree of saturation. Changes in mineral stability may provide pathways for increased groundwater movement, and changes in sorption characteristics affecting repository performance.

!! strange wording.
*

MEASURING ALL THE REACTIONS/PROCESSES/CONDITIONS CALLED FOR IN THIS SECTION MAY BE ALMOST AN IMPOSSIBLY LARGE JOB!

ISSUES

WHAT ARE THE ANTICIPATED GEOCHEMICAL REACTIONS/PROCESSES/CONDITIONS AFFECTING RELEASE AND TRANSPORT OF RADIONUCLIDES TO THE ACCESSIBLE ENVIRONMENT? The concepts of emphasis of key radionuclides,

i.e., main contributors to release, and use of bounding and limiting conditions

Geochemical reactions, processes, and conditions at the waste package surface, in the backfill, the disturbed zone, and the far field will affect the release and transport of radionuclides from the repository and the accessible environment; and thus play an important role in assessing performance issues 8,9, and 10. Release involves waste package degradation and solubilization of the radionuclides in the waste form. Transport involves any mechanical or chemical process which promotes or inhibits radionuclide migration from the repository to the accessible environment. During release and transport, radionuclides will react with the groundwater, the waste container, backfill and the host rock, and the nature of these reactions will determine the extent of the migration of each radionuclide in the waste form.

and values should be included to help keep work needed for a realistic level.

apparent concentration limit?

3.3.1 What is the expected solubility of released radionuclides in the near-field and the far-field through time?

The rate at which radionuclides are transported to the accessible environment is a function of solubility, the rate and path of groundwater movement, and the reactions of radionuclides with minerals in the

concentration really → solubility is a
11 ~~catching~~ ~~hand~~ ~~little~~ ~~secret~~ ~~cool~~

see
XREF

backfill, in fractures in the host rock, and in the host rock itself. Dissolution of radionuclides from the waste form into solution is controlled by the physical ^{+ chemical} characteristics of the waste (e.g., structure, and surface area), ^{ok} chemical and radiolytic properties of the waste, composition, redox conditions and the pH of circulating waters, temperature, and pressure. Under slow flow or no flow conditions a conservative estimate of concentrations of radionuclides species released into solution is that they are solubility limited. There-
 fore, in order to determine the concentrations of radionuclides in the near-field and the far-field (under different geochemical conditions) through time, their solubilities need to be determined.

~ = unrealistic delete?
 ignores colloids and particulates

400 conditions

3.3.1.1 How does precipitation/co-precipitation affect radionuclide solubility concentration?

REDAUNDANT

Under varying geochemical conditions, radionuclides in solution may precipitate in the presence of certain inorganic ligands (e.g., carbonate, hydroxyl, sulfide). Parameters controlling precipitation include groundwater composition, rock composition, redox conditions, and pH. Certain radionuclides may co-precipitate by substitution with non-radioactive species such as iron. *interstitial substitution*

3.3.1.2 How does speciation affect radionuclide solubility/concentration?

does this mean BWIP is supposed to identify all radionuclide species? That's almost impossible!
 The identities and solubilities of the solid phases, and identities of the solution species likely to form under geologic conditions are needed in order to determine solution concentrations of radionuclides in a repository groundwater system. Different species of the same element will remain in solution in different concentrations and migrate at different rates.

I disagree

AWK

3.3.1.3 How do colloids affect radionuclide solubility/concentration?

others can ion exchange onto active silica surfaces

Some radionuclides, especially hydrolyzable ones may readily form colloids or pseudocolloids under certain geochemical conditions. These colloids may result from interactions with the waste package. The formation of colloidal species may affect the concentrations and thus the migration of radionuclides in solution.

3.3.1.4 How do organics affect radionuclide solubility/concentration?

Sounds like 2 radionuclides complexing with one another.

The presence of certain organic ligands can allow some radionuclides to form complexes and remain in solution at concentrations (different) than uncomplexed species. generally much higher

3.3.2 How do chemical changes in the outermost packing material and the mineralogies of the backfill, and the near-field, and far-field host rock influence radionuclide migration through time?

→ geochemical chemistry

Chemical changes in the packing material due to temperature, pressure, and saturation will affect its ability to retard mobile radionuclide species. Highly sorptive minerals in the backfill, near-field, and far-field host rock may cause significant retardation of radionuclides. A good estimate of the location, volume, and accessibility of minerals along the likely flow paths is necessary to assess the effects of mineralogy on radionuclide migration and retardation.

3.3.3 How will reaction and sorption kinetics affect radionuclide release and transport?

The occurrence of reactions is predicted by chemical equilibrium. However, reaction rates are generally not instantaneous as predicted by equilibrium, but kinetically controlled (time dependent). Thus, rate information is necessary in order to predict reaction rates and the steady state conditions expected in the repository system.

if really necessary to predict reaction rates? this will be tough!

use of sorption ratio values is conservative if rates are slow and sorption/desorption disequilibrium occurs

3.3.4 How do redox conditions affect radionuclide mobility?

Redox conditions ^{can} ~~will~~ be a significant determinant of radionuclide speciation, solubility, and migration. Construction of a repository will allow atmospheric oxygen to enter into the repository horizon and cause oxidizing conditions. After closure, the atmospheric oxygen may be consumed and redox conditions should return to or approach ambient ^{conditions} (neglecting radiolytic effects).

does not affect all radionuclides.

3.3.4.1 What are the effects of gamma and alpha radiolysis of ^{many other conditions} ~~redox~~ conditions?

may generate stable organics from CH₄ in groundwater

There is evidence that radiolysis may affect redox conditions, causing generation of hydrogen, oxygen, and other species, and thus affect anticipated reactions. These conditions may influence radionuclide speciation and transport.

solubility/adsorption

3.3.5 How does diffusion affect radionuclide migration/retardation in the near-field and the far-field through time?

At relatively low groundwater velocities, chemical diffusion is the dominant process for solute transport. Diffusion is driven by a concentration gradient rather than a head gradient. Under very slow water velocity conditions, diffusion could be a significant process for radionuclide retardation.

More important if groundwater flows "rapidly" through fractures.

3.3.6 How do colloids/particulates affect radionuclide migration/retardation in the near-field and the far-field through time?

Under certain geochemical conditions, radionuclides may form colloids, pseudocolloids, or particulates. Colloids and particulates are potentially more mobile than aqueous species formed under the same conditions. The stability and mobility of colloids and particulates under changing geochemical conditions need to be addressed in evaluating radionuclide retardation.

~ = should explain.

? I don't understand significance of this issue -- could be included in some discussion elsewhere

← "hydrocarbons" a better word?

3.3.7 How do organics affect radionuclide migration/retardation in the near-field and far-field through time?

Organics may be introduced into a repository during construction by contamination from the surface or from the host rock itself, (usually in interbeds.) Radionuclide organic complexes ^{can} have different migration behaviors than inorganic complexes. The likelihood of significant amounts of organics being present for complexation with radionuclides and radionuclide complex migration behavior should be addressed.

don't forget radiolysis effects here

is this true in basalt?

at the RRL hole the system appears to be saturated with CH₄ at T and P.

APPENDIX A

TECHNICAL AND REGULATORY IMPORTANCE OF GEOCHEMISTRY

The importance of geochemical parameters can be described in two contexts: technical and regulatory. The technical importance involves the relationship between repository geochemistry and the overall purpose of the repository, which is to prevent hazardous levels of radionuclides from reaching the accessible environment. The regulatory importance involves the relationship between repository geochemistry and the need to show that the repository meets applicable regulations and criteria.

A.1 Technical Importance

The geochemistry of a radioactive waste repository is important in two areas: (1) the chemical interactions of the rock/groundwater system ^{with?} and the waste ^{"and" doesn't make sense} package components will be largely responsible for the degradation and failure of the package and subsequent release of radionuclides, and (2) the chemical interactions of the egressing radionuclide-bearing groundwater will control the extent to which the radionuclides remain soluble and the sorption retardation which limits the quantity and relative rate at which they are transported to the accessible environment. The impact of groundwater on the waste package involves considerations such as the characteristics of the unperturbed ^{ambient?} (before emplacement) groundwater and the effects of altered conditions (e.g., temperature, radiation) and materials (e.g., backfill, canister) on these characteristics. The altered groundwater characteristics are important, because they control the chemical ^{mineralogical} alteration of the packing materials surrounding the waste package, and eventually the rate at which radionuclides are taken into solution and transported from the waste form. Thus, geochemical considerations affect the mobility and transported rate of radionuclides by controlling the degree to which various elements are soluble in the groundwater, the extent to which the transport of solubilized radionuclide elements is retarded by sorption, and the possibility that radionuclides could be transported by colloids, supersaturated solutions, particulates, or organic complexes. } Verbose.

A.2 Regulatory Importance

The regulatory importance of the geochemical aspects of a radioactive waste repository derive from Title 10, Part 60 of the Code of Federal Regulations (10 CFR 60), entitled "Disposal of High-Level Radioactive Waste in Geologic Repositories Technical Criteria." These criteria include the EPA standards contained in Title 40, Part 191 of the Code of Federal Regulations (40 CFR 191), that are currently being circulated in draft form for comment. Geochemical evidence will be used to support virtually all technical or scientific considerations in these regulations.

The specific parts of these regulations involving geochemistry are discussed below with reference to the pertinent portions of 10 CFR 60.

1. Sect. 60.112 -- This section requires that the repository meet applicable EPA standards, i.e., 40 CFR 191. In general terms, this standard places an upper limit on the amounts of radionuclides that can be released to the accessible environment. The accessible environment includes the atmosphere, land surfaces, surface waters, oceans, and parts of the lithosphere more than 10 km in any direction from the original location of any of the radioactive wastes in the disposal system. Limits are placed on both "reasonably foreseeable releases" (more than 1% chance of occurring in 10,000 years) and "very unlikely releases" (less than 1% chance of occurring in 10,000 years).

It is anticipated that the geochemical aspects of a repository will be important in showing compliance with these standards because hydrologic considerations alone do not appear adequate to demonstrate compliance in many situations. The geochemical aspects of relevance here are the limiting solubility and sorption of the radionuclides and the processes and effects that can circumvent these radionuclide transport retardation mechanisms. These aspects are, in turn, controlled by the overall geochemistry of the repository system, especially groundwater composition and the reactions expected under perturbed repository conditions.

2. Sect. 60.113(a)(1) -- This section states the NRC criteria concerning the engineered barrier system (principally waste package) performance. This system must be designed so that, assuming anticipated processes and events, there is reasonable assurance that (a) containment of the radionuclides^x within the engineered barrier system will be substantially complete for a period ranging between 300 and 1000 years, and (b) that radionuclide releases rate after this containment period will be no greater than 10^{-3} /yr of the radionuclide inventory calculated to be present 1000 years after the repository closure. The radionuclide release rate limit is at the boundary of the engineered system, which is interpreted to mean the waste package-unmoved rock interface.

The geochemical aspects of the repository are important in showing compliance with this criteria because the dominant failure modes of the waste package components are expected to result from aqueous corrosion mechanisms and the rate of corrosion is controlled by the amount and composition of the groundwater. Thus, groundwater characteristics such as chemical constituents, pH, flux and redox conditions, both undisturbed and altered, are directly relevant to the performance of the waste package.

corrosion of bentonite? *

alteration/corrosion

Temperature

3. Sect. 60.113(a)(2) -- This section, which involves geochemical aspects only directly [see Sect. 60.113(b) below], sets forth the criterion of a minimum 1000 years pre-waste emplacement groundwater travel time from the disturbed zone to the accessible environment.

4. Circumstances under which the NRC can specify values other than those contained in the criteria in sect. 60.113 (see items 2 and 3 above). Among the factors that the NRC may take into account is "The geochemical characteristics of the host rock, surrounding strata and groundwater..." [Sect. 60.113(b)(3)]. Thus, a repository site having superior geochemical attributes, such as low solubility and high sorption, could be allowed to relax the performance objectives put on [?]engineered system and hydrology. Therefore, in those cases where DOE repository projects petition to make some or all of the performance criteria less stringent, it is expected that the geochemical setting would be the principal basis for any Performance Objective exception request.

Why the 'caps' here and A-18 not here?

5. Sect. 60.122(B)(3,4); Sect. 60.122(C)(7,8,9,10) -- These criteria outline both favorable and potentially adverse conditions relevant to siting an HLW repository. Favorable conditions: (a) promote radionuclide precipitation and/or sorption, and (b) inhibit the information and transport of radionuclide colloids, particulates, and complexes. Potentially adverse conditions include: (a) geochemical conditions and processes that could increase solubility and/or waste package degradation or reduce radionuclide sorption, (b) conditions in the saturated zone that are not reducing, and (c) evidence of dissolution. These favorable and potentially adverse conditions are to be considered in the context of providing reasonable assurance that the other criteria and standards discussed above will be met. Thus, the geochemical aspects of the repository identified in items 1, 2, and 4 are pertinent here.

*

*

talk about "baseline characteristics," just say "geochemical conditions."

APPENDIX B

GEOCHEMISTRY INFORMATION NEEDS

B.1 Geochemical Data Needs

Use of the word "baseline" here is different than on p. 7 where it refers to ambient conditions, processes, etc.

If so, then why

There are two different classes of geochemical information of interest in the context of an HLW repository: baseline characteristics and derived data. The baseline characteristics are the geochemical conditions in the repository that control or affect chemical processes. These are important because (a) they directly impact the performance of the HLW package, and (b) the interaction of these conditions with released radionuclides would determine the extent to which they are solubilized and the degree to which their migration is retarded via sorption. The ^{line}base geochemical conditions include: groundwater

~ = pertinent to?
peculiar wording.
wording could be improved.

is mean
clearer
is unclear,
not
geochemical
conditions,
if this
not
idea from
a sentence
structure.
this sentence
could be
rewritten.
maybe it
is not
clear at
all.

composition (undisturbed and altered), temperature, pressure, pH, redox conditions, and the petrology/mineralogy ^(undisturbed & altered) along potential release pathways.

Sounds funny.

The derived data are geochemical manifestations of the interactions of the geochemical conditions with the repository and environs. In general, these are the parameters that characterize the rate at which radionuclides can migrate from the repository and thus are employed as input to repository performance assessments. The most heavily derived parameters are the ^{limiting} solubility and sorption of the radionuclide elements. Other parameters of interest involve colloid formation, particulate transport, kinetic limitations, and radionuclide speciation.

"release" also
retardation processes:

The NRC will evaluate the degree to which DOE has identified "information that is not available because of unresolved scientific, engineering, or technical questions." The DOE, ultimately, will facilitate the task of evaluating the adequacy of the data in quantitative terms by assigning relative degrees of importance to the data. The NRC will take a position on data quality and reliability of data collected by the DOE when DOE has indicated what credit it intends to take for various data in a license application.

Aren't these "parameters" really just radionuclide transport and retardation processes?

When considering some of the geochemical variables that can affect repository performance, including temperature, pressure, ~~Et~~ pH, groundwater composition,

redox conditions

radiation, colloid formation, solid substrate characteristics, and that these variables change with time and space, several questions may arise:

- How many variables exist that can determine geochemical aspects of repository performance?
- How many combinations of these variables can exist when they all vary at the same time? *Makes no sense to me.*
- How much information is needed for a license application?
- By what process will necessary data points be identified? *Wouldn't "sets" be a better word.*

The significance of the parameters in repository performance must be taken into account. Obviously, more needs to be known about features that are critical to performance than about features that are less critical. To some extent, judgement and experience lead to identification of the more important components and the specific parameters which must be measured to obtain at least a general understanding of system component performance. It is impractical, however, to rigorously derive and prescribe meaningful, quantitative performance requirements before site characterization. This is due to the combination of a high level of uncertainty in both site information and understanding of relationships between system components together with the lack of finely developed site-specific performance assessment methods. For example, as documented in the NRC staff analysis of the BWIP SCR, the uncertainty in such fundamental parameters as groundwater travel time ranges over nearly six orders of magnitude. The ^{minimum} ~~maximum~~ travel times are on the order of several tens of years (i.e., far less time than needed for the waste to decay to innocuous levels) to a ^{maximum of} million years. *(This example doesn't seem relevant)*

The NRC considers that in spite of the lack of a large data base to support rigorous assessments, there is still a sound basis for identifying primary information needs sufficiently well to begin a program of investigations. The basis upon which primary information needs are identified is the identification of the performance assessment methods that will be used to determine compliance

use
and
base.

~ = base
knowledge
is not the
same as
uncertainty

Isn't
this a
hydrology
issue?

→
E
pository
projects
are
already
well underway.

~ =
Repetitive

many of these can be identified until basic data is obtained.

of the repository system of natural and engineered barriers with 10 CFR 60 requirements. Specific data needs can be identified from consideration of the performance assessment methods, including scenarios and associated conceptual mathematical models that will be used, the simplifying assumptions underlying the methods, and the need input parameters to such models. By considering specific assessment methods in a systematic way (e.g., using decision tree analysis) together with some limited quantitative sensitivity studies and scientific judgement, the relative importance of information needs may be established.

Verbose.

Quantitative sensitivity studies will be attempted by both NRC and DOE to identify the degree of precision required in data. These studies should be performed at several different levels: at the overall system level as well as at the level of individual system components, or at a level which evaluates selected important aspects of the program such as groundwater flow. These studies should allow for the full range of uncertainties existing with respect to each parameter and in the model themselves.

*

Improper English.

In view of the lead role of the DOE in gathering data (as prescribed in the Act) and assessing relative amounts of credit it will take for data in a license application, NRC will assess independently, through sensitivity analyses, the relative significance of conditions and processes affecting repository performance. For example, although NRC cannot prescribe accuracy requirements before DOE has developed specific testing plans and indicated how much reliance it will place on certain data, NRC can provide guidance to DOE during site characterization planning and investigations through assessing the impact of numerical values in selected performance criteria of 10 CFR 60 on compliance with the EPA standard.

Verbose meaning unclear

same com this also

In adhering to the intent of the Act, the NRC has adopted a systematic, iterative approach to identification of the data and the quality of data required for licensing during the interim period following site screening and prior to detailing site characterization.

*

= poorly worded.

The initial element in the systematic, iterative process is to establish the present level of understanding about the site. This is followed by the identification of the performance issues which eventually must be addressed to

This sentence says almost the same thing that is said in the last sentence on p 8-21. Therefore, this commentary is repetitious.

determine whether the site and the engineered system will comply with NRC regulations. These issues are the basis for the development of specific assessment methods including conceptual, mathematical, and numerical models. Inputs and assumptions to these models help determine the information needs that must be addressed during site characterization.

Similar commentary appears on the top of p. B-22.

Of all the steps in the iterative process, overall system and component level sensitivity studies are a critical element since they can be conducted at several levels using a variety of methods to determine what are the essential information needs.

Obtuse and verbose.

In some areas, it is also necessary for DOE (and NRC) to establish initial (preliminary) component requirements in parallel with the development of assessment methods and sensitivity studies. These requirements should evolve along with the program and therefore will be adjusted as the whole process is repeated when new information or methods are developed. The nature of many of these requirements can be inferred directly from the performance issues, and, once they have been established, they also make an essential contribution to identifying information needs. Acceptable levels of uncertainty are also established here, and directly affect the amount performance contributions (trade-offs) are adjusted to compensate for uncertainties in various components.

why? DOE decisions + needs requirements for components

Improper sentence structure

Obtuse and verbose

The elements described up to this point all contribute to identifying issues for which information will be needed. Once these issues have been identified, the establishment of test plans and procedures follows directly and forms the basis for generating data and determining the uncertainties associated with them. These data and uncertainties can be then used to upgrade the sensitivity studies and the assessment methods and refine the component requirements. This process by its nature must be an evolving, iterative one. It must start with the use of substantial judgement, relatively simple models, and sparse information. As the program proceeds and more data are gathered, the process and its steps will become more refined until acceptable level of uncertainty can be reached and finding made.

Are there issues for which information is not needed?

This has been stated previously.

How about a simplified flow-chart to help visualize this process. -- I think the essential elements are here, but they are lost in some of the wording.

B.2 Programmatic Considerations

One of the key factors to be decided in obtaining geochemical information is the degree to which understanding of a particular geochemical process is needed or required. One of the spectrum (understanding) would require essentially complete mechanistic understanding of each geochemical process to be employed for each element through location and time. For example, if plutonium solubility limits were to be employed in support of repository licensing, then the solubility of plutonium species and any other interacting elements would have to be understood sufficiently to permit solubility values to be synthesized for relevant repository conditions. The other end of the spectrum (knowledge) would require only that the relevant parameter (e.g., plutonium solubility) be obtained under relevant conditions and that some assurance be available that the value is conservative through time. This type of information acquisition would likely be the result of a large, integral experiment (laboratory or in situ) instead of being synthesized from detailed mechanistic data. There are, of course, various intermediate combinations of the two approaches. Cursory analysis of these two approaches indicates that the amount of work required to "understand" all of the aspects of each geochemical parameter to be employed in repository licensing is far greater than that required investigation of a wide variety of species, processes, and conditions in order to ensure that no significant effects have been ignored and to fully quantify these effects. Thus, an "understanding" of geochemical parameters is not generically required, and will only be necessary if needed to show that the values obtained are representative or conservative.

A persistence issue concerning geochemical repository parameters is whether the parameter values must be expressed probabilistically (i.e., as a probability distribution function) as opposed to deterministically (i.e., a single value or a range). It is clear that many radionuclide transport and waste package performance assessment methodologies employ probabilistic methods, typically involving sampling from probability distribution functions (PDFs) for the input parameters.

of
did/should/shouldn't

A sentence

wording should be improved.

Sounds like a non sequitur to me.

~ = Strange wording.

This type of work can be VERY

time consuming

good approach!

this statement doesn't seem to be related to the "issues"

Complete utilization of these methodologies would indicate that the geochemical parameters should be available in the form of PDFs. On the other hand, the generation of enough data to formulate reasonably accurate PDFs for the large number of geochemical variables in a complex, interdependent geologic system requires a very large amount of resources and time. Thus, the data needed for determining PDFs may not be necessary if the conservative end of a range of values fulfills the data requirements.

In the context of this section, "bounding value" *is meant to denote* that the result employed in the performance analyses will be representative of the conservative end of the range of values for a particular parameter and that reasonable assurance is available that this is, in fact, the case. A conservative bounding value is not meant to imply that absolute limiting values need to be employed or that absolute assurance must be given that values less conservative than the bounding value will never manifest themselves. For example, the best-estimate solubility limit for plutonium under certain geochemical conditions may be, say 10⁻¹⁰M. However, if the range of plutonium solubilities under the varying geochemical conditions anticipated along the flowpath range from 10⁻¹²M to 10⁻⁸ M, and experimental and calculational evidence or theoretical arguments indicate that values are unlikely to fall outside this range, then the 10⁻⁸ M value would constitute a conservative bound, appropriate for use in performing analyses. To continue the example, the use of a bounding value does not mean that plutonium has to be assumed to be infinitely soluble.

Somewhat redundant.

} Clearly, this is a different example.

It should be noted that, for many parameters, it may not be immediately evident which end of the range is conservative, or the effect of varying a parameter may be conservative or nonconservative, depending on the situation. In these cases, obtaining a deterministic bounding value will require that both ends of the range be bounded and that sensitivity studies be conducted to examine the impacts of parameter variability.

It is *theoretically possible* to calculate some of the values for geochemical parameters such as geochemical conditions, solubility, and *sorption*. In practice, attempts to calculate geochemical values have been restricted to the

most people disagree

determination of solubility values and, occasionally, a limited set of geochemical conditions. The input to these calculations comprises (1) thermodynamic data for all of the ^{important ones only} potential species in solution and solid materials in the system, and (2) some geochemical conditions, the number of which depending on the type of calculational approach employed. Although these methods have been employed to calculate solubility values for use in analyzing the performance of HLW repositories, they are known to suffer from the following deficiencies:

1. The minimum condition for acceptable results is that the thermodynamic data base be both complete and accurate. Obtaining accurate thermodynamic data ^{is} a time-consuming process. The completeness of the thermodynamic data base cannot be conclusively demonstrated, since it is ^{always} possible that an important, but presently unknown species will manifest itself and significantly change the results.

of tryp
or actinides

How complete
and accurate
that is the
question.
*

2. The currently existing calculational methods assume that the geochemical system being presented is in equilibrium and that equilibrium (different from the beginning) will be maintained throughout the perturbations introduced by the construction of the repository and the emplacement of the waste. Kinetics would suggest that this would not be true for all reactions and, ^{in fact}, experimental evidence has shown that many natural systems are not in equilibrium with respect to their major constituents even after millions of years.

However, metastable equilibrium, manifested by steady-state conditions, may be commonplace.

The situation with respect to calculation of sorption values is much less sophisticated ^{as a result of} (1) the fact that "sorption" is a really combination of chemical ^{and physical} mechanisms, and (2) the lack of a firm theoretical basis for the calculational approach. Thus, the values obtained from such calculations to-date have been uncertain estimates at best and, as a result, have found little application in providing input to repository performance assessments.

OK

good approach!

not possible for all parameters

radionuclides inventory calculations

As a result of these considerations, the values obtained as a result of theoretical or semi-empirical calculations are not acceptable for use as input to repository performance assessments, unless the results have been experimentally verified under conditions within the range of those anticipated in the HLW repository. However, the geochemical parameter values obtained from experiments simulating anticipated repository conditions are acceptable for use as input to repository performance assessments, subject to peer review, and independent reproducibility for quality control purposes.

Science structure and wording could be improved.

precautions?

Revised: words like people will be computing for 10,000 years.

longer not a clarity.

Demonstrating compliance with applicable regulations will require assessment of waste repository performance over a time span of at least 10,000 years. Thus, it will be necessary to provide geochemical values for input to the performance assessment over the same time frame. Clearly, it is impossible to perform real-time experiments to measure the required values. Additionally, as noted earlier, calculated geochemical values that cannot be verified experimentally have such greater uncertainties that their validity is not reasonable assured. Acceleration of experiments does not appear feasible since the required accelerations (presumably brought about the temperature increases) would be so large that there would be no assurance that the geochemical processes would be the same as those that would actually occur. Therefore, the extrapolation of geochemical values obtained as a result of short-term experiments should be accomplished by identifying conservative bounding values for the necessary parameters and use of analogs. This identification can be accomplished by (a) invoking theoretical arguments to supplement the experiments or calculations, and/or (b) employing sensitivity studies to show that there is reasonable assurance that projected repository conditions do not result in geochemical parameters assuming values that result in unacceptable performance. An example of the first option would be to experimentally determine the solubility limit for radionuclides in a short-term experiment and to justify using this limit over the long term by showing thermodynamically that the radionuclides with either retain that solubility limit or react to form species having lower (and, thus, more conservative) solubilities.

validated? YES

wording could be improved.

some degree of acceleration is unavoidable

some informative examples?

Working should be improved.

Demonstrating the validity of the geochemical values to be used as input to repository performance assessments requires that the values be reproducible and accurate. Reproducible means the different investigators should be able to calculate or measure the same value using the same methods or by employing different methods that should theoretically lead to the same result (e.g., a different experimental technique or a different numerical method). Acceptable methods for showing reproducibility include repetitive experiments and calculations, alternative experimental and calculational methods, and independent round-robin tests involving well-established protocols.

} What about conservative values? These values may not be reproducible or accurate.

... but; since repetitive tests may all sub from same problems.

The accuracy of geochemical values is related to the degree to which the method use to obtain the values represents the actual situation which the experiment or calculation is intended to simulate; i.e., the extent to which the results conform to reality. The accuracy of geochemical values (or any other values) relevant to a HLW repository is the basis on which the entire performance assessment rests ^{because} since the predicted performance can be no more accurate than its input data. Unfortunately, demonstrating accuracy of any experimental or calculational method requires ^sindependent observations ^sof the "real" system over the time frame of interest and under the conditions of interest for absolute certainty. This is clearly impossible in the case of a HLW repository. Thus, reasonable assurance of accuracy will have to be the result of ^{obtained from} comparisons with ^{between} somewhat-similar natural analogs, conformance to expert opinion, and the extent to which the results can be satisfactorily rationalized/explained.

*

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