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FROM: Nancy Still
Docket Control Center, WM

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SUBJECT: UPDATES TO SIA'S FOR BWIP DSCA (NUREG-0960)

Enclosed are updates of Site Issue Analyses (SIA's) for the
BWIP Draft Site Characterization Analysis (NUREG-0960).

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Enclosure:
As stated

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PDR/LPDR

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Issue No. 3.1

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

2. Statement of Issue:

What is the expected solubility of released radionuclides in the near-field and the far-field through time, excluding the waste package?

3. Importance of the Issue to Repository Performance

The quantity of radionuclides transported to the accessible environment will be determined by their solubility, the volume and path of groundwater movement and the reactions (sorption) of the radionuclides with minerals in the backfill, in fractures in the host rock, and in the host rock itself. Theoretical analysis of potential solution species and solubilities (under reducing conditions) suggest that radionuclides are likely to be in solution at levels that limit their release to the accessible environment to permissible levels. Therefore, the determination of radionuclide aqueous speciation and other supporting thermodynamic data are necessary to assess the importance of solubility in controlling radionuclide migration over the time frame of thousands of years for the conditions to be expected.

4. Portions of 10 CFR 60 that are directly connected to the Issue

60.113 Performance of particular barriers after permanent closure

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

60.122 Siting Requirements

(b) Favorable Conditions

- (1) The nature and rates of tectonic, hydrogeologic, geochemical and geomorphic processes operating within the geologic setting during the Quarternary Period would not affect or would favorably affect the ability of the geologic repository to isolate the waste.
- (4) Geochemical conditions that -- (i) promote precipitation or sorption of radionuclides; (ii) inhibit the formation of particulates, colloids, and inorganic and organic complexes that increase the mobility of radionuclides; or (iii) inhibit the transport of radionuclides by particulates, colloids, and complexes.
- (5) 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.

(c) Potentially adverse conditions

- (9) Groundwater conditions in the host rock, including chemical composition, high ionic strength or ranges of Eh-pH, that could affect the solubility of the waste form or chemical reactivity of the engineered barrier system so as to increase the difficulty of designing the engineered barrier system to meet the performance objectives of Sects. 60.112 and 60.113.
- (11) For disposal in the saturated zone, groundwater conditions in the host rock that are not reducing.

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

A major mechanism for controlling release of radionuclides from a repository in basalt is the precipitation or incorporation of radionuclides into new mineral phases, i.e., solubility constraints. Assuming steady state conditions, radionuclide solubilities can be used to calculate the maximum possible concentrations

and therefore release, of a radionuclide in a specific system. Radionuclide solubility, like sorption, is highly dependent on environmental parameters such as Eh, pH and groundwater composition (JACOBS 1981). At this time, there are few experimental solubility data available for conditions relevant to a repository in basalt, particularly at elevated temperatures. Based on available thermodynamic and laboratory data, solubilities have been estimated for the basalt geohydrologic system (SALTER in press). These solubility estimates show that under reducing conditions anticipated for basalt, UO_2 and $USiO_4$ have solubilities on the order of 10^{-8} moles/L, whereas NpO_2 and SeO_2 have solubilities of approximately 10^{-15} moles/L.

Dissolution of the waste form (solubilization) leads to the question of whether an element that has been released from a solid phase will remain in a groundwater as a dissolved species (MOODY 1982). Speciation is a function of groundwater characteristics, temperature, pressure and interactive effects between the aqueous phase and any solid along the transport path (SIAs 3.8 and 3.9). The ground-water characteristics also determine whether the element will occur in solution as a simple or complex ion. The level of knowledge about speciation and the amount of thermodynamic data needed to calculate a solution chemistry, not only at $25 \pm C$ and 0.1 MPa, but also at increased temperature and pressure, is highly variable for each element. Reasonably complete data bases are available for all elements except Tc, Pu, Np, Am, Cm, Se, Pa, Ru, Pd, Sr, Zr, and the rare earth elements (see e.g., LANGMUIR 1978; FUGER 1976; PHILLIPS 1982; PHILLIPS in press; LEMIRE 1980; BENSON 1980), many of which are important in repository assessment. Most studies have demonstrated that uranium and actinide ions, regardless of valence state, tend to form complexes of varying stability in aqueous solution with all major ligands found in groundwater (e.g., CO_3^{2-} , F-, PO_4^{2-} , SiO_4^{2-} , Cl^- , OH^-). Relationships between dissolved ionic species and possible natural amorphous or crystalline phases which can precipitate from ground waters have been calculated assuming equilibrium for both general geologic environments (Rai 1978) and for basalt aquifers in the Columbia Plateau (DEUTSCHE 1982).

Precipitation of a radionuclide can occur forming, for example, insoluble oxides, hydroxides, carbonates, sulfates, phosphates, silicates, and sulfides. In addition, radionuclides can co-precipitate in minerals formed during alteration of the backfill or the host basalt itself. Except for some data on Th and U (LANGMUIR 1978; LANGMUIR 1980), thermo-dynamic information on the complex mineral phases the actinides might ultimately form, or the partitioning of trace actinides into phases formed as a consequence of waste/basalt/groundwater interaction, are nonexistent.

Radionuclides can also precipitate out of the groundwater as extremely fine-grained colloids (ALEXANDER et al. 1977). Many highly charged cations have a tendency to form polymeric hydroxides. This is particularly true for tetravalent actinides (JOHNSON 1978). Hydroxy colloids may be regarded as highly polymerized species with large residual charges that do not aggregate because of electrostatic repulsion. Thus, an apparent solubility which can exceed the solubility product may be achieved. Work summarized in BENES 1980, OLOFFSON 1982, and STARIK 1961 has shown that actinide colloids have a strong tendency to sorb on exposed mineral surfaces in the neutral to slightly acid pH range. However, at high pH as expected in the basalt repository (JACOBS 1981), stable species can be formed that carry a residual negative charge, leading to a decrease in their sorption.

6. Summary of the Information Needed to Closeout the Issue by the Time of Construction Authorization

The following areas (in order of priority) should be addressed before the issue can be closed out:

- (a) The equilibrium constants (or free energies) used in solid-solution modeling should be measured for conditions dominating the basalt repository environment and the reliability of the values validated. It is quite common for experimental solubility product constants and complex formation constants to vary by 1 to 3 orders of magnitude. Quite clearly this amount of uncertainty can cause large differences in the computed results and probably contributes the largest single source of error.

- 7
- (b) Since solubilities are in general a function of temperature, efforts should be directed toward measurements of solubilities as a function of temperature and pressure for critically important solid phases and aqueous species.
 - (c) The mechanisms leading to the formation of colloids and their influence on solubility in waste/basalt/groundwater interactions are, at present, poorly understood and should receive more attention. Measurements are needed on the nature, radionuclide content and migration properties of colloidal forms produced through degradation of proposed high level waste forms. In addition, the nature, concentrations, particle size distribution and migration properties of naturally occurring colloidal material suspended in the subsurface waters should be evaluated.
7. Summary of the Planned Approaches to Testing, Test Methods, and Investigations to Provide the Information Needs of (6)

In order to overcome the handicap of a limited data base, the BWIP proposes to experimentally measure the solubilities of compounds of uranium, plutonium, americium, and other key radionuclides under the exact site-specific conditions anticipated to occur in the basalt repositories (i.e., low Eh (less than 0.0 v), high temperature, moderate pressure, high radiation field, and complexing ligands). Specifically, they intend to:

- (1) continue experiments already initiated on the interactions between the waste form, basalt and groundwater over the temperature, pressure, and Eh-pH conditions expected for the repository (near-field),
- (2) use data supplied by other laboratories from long-term static and low flow rate dynamic leach tests on simulated spent fuel and borosilicate glass,
- (3) experimentally identify the dominant radionuclide species in basalt groundwater,
- (4) evaluate conditions that could lead to possible radionuclide colloid formation and subsequent particulate transport,

- (5) investigate the possible effects of the radiation field on radionuclide geochemical behavior (H₂O radiolysis to H₂, H₂O₂, etc.)

The solubility, speciation and colloid data will be coupled with an uncertainty analysis to insure the successful prediction of radionuclide concentration ranges in the basalt groundwater.

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

The plans in the Site Characterization Report for determining solubilities, speciation and colloid transport are not detailed enough for the NRC to assess whether they are adequate. This statement is based on the following observations:

- (1) A detailed description of experimental and analytical techniques is not provided. In order to characterize solubilities, experiments should be bracketed by coming from both under- and oversaturation.
- (2) A decision on which radionuclide compounds are to be used in the solubility experiments is not provided. In addition, it is not clear whether they will examine the compounds one at a time, or as aggregates.
- (3) They are considering only reducing conditions in their experiments. They should also consider oxidizing conditions which may be encountered in the near-field immediately after waste emplacement or in the far-field environment, both in the basalt and the interbeds.
- (4) No strategy was given for determination of the speciation of critical radionuclides. Speciation can be determined from solubility experiments, spectroscopic analysis, acid-base potentiometric titrations and polarography. Calculations to date have considered only simple oxide species.
- (5) The types of colloids expected to form are not discussed (e.g., oxides, hydroxides, oxyhydroxides, organics). Colloids can form from solution as the result of oversaturation or from physical degradation of the basalt or waste (i.e., particulate exfoliation).

- (6) The expected influence of the radiation field on radionuclide behavior at high pressure-temperature is not discussed.
- (7) The methods of insuring compatability between BWIP data and data generated by other labs trying to simulate the in situ conditions of the basalt repository are not described.
- (8) There was no discussion concerning the methods of assessment of uncertainties on existing data or data to be obtained.
- (9) The development of computational schemes required to address solubility, speciation, and colloidal transport in a complex fluid flow regime was not considered.

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Issue No. 3.2

[Mr. CROFF:

NOTE: some text missing from transmission beginning of issue 3.2.]

tion of the rock strength, or adversely affect the performance of the engineered barrier system.

(11) For disposal in the saturated zone, groundwater conditions in the host rock that are not reducing.

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

Backfill is the material used to fill the engineered system cavities after waste emplacement. It probably will consist of more than one component in order to meet the dual requirements of restricting the movement of groundwater to the waste canister and of retarding radionuclide transport after a canister-breach -- groundwater-intrusion event (BEALL 1982); (WOOD 1982a). The materials presently under consideration are sodium bentonite and crushed basalt. Bentonite has good swelling properties in water under ambient conditions, and work is under way to study its properties at the elevated temperatures to be encountered in the near-field thermal pulse (SCR 1982). The repository host rock has favorable radionuclide migration retardation properties, and application of crushed basalt (which will be readily available from repository mining operations) is being considered as a backfill material (WOOD 1982b). Uncertainties include the undetermined stability of bentonite to be expected at the thermal and radiation levels to be encountered in the near-field. If the bentonite crystal structure is altered by these conditions, then the desirable swelling properties which restrict the movement of groundwater could be lost with time. The effect of crushed basalt on radionuclide migration is being quantified (WOOD 1982b).

Uncertainties may include the not completely defined ability of the crushed basalt to achieve satisfactory radionuclide retardation under near-field conditions. Basalt may have little effect on some anions such as iodine, and the use of additional backfill components specific for anion retardation may need development (BEALL 1982).

The near-field mineralogy influences radionuclide migration by helping establish the parameters such as Eh, pH, solute composition and surface properties that control the geochemical process of sorption involved in radionuclide retardation. The near-field minerals include those in the host rock component of the engineered system. The near-field mineralogy and its influence on radionuclide retardation will be similar to that in the far-field. It will be different from far-field behavior primarily in that higher temperatures (250-300±C) and radiolysis products will be involved. Only limited information on the near-field waste package/groundwater/backfill/basalt reactions is available (BENSON 1979); (SCR 1982). Uncertainties in the waste form, waste load, canister material(s), and backfill component(s) make a definitive analysis of near-field radionuclide retardation difficult at this time. As the engineered system becomes better defined and the system parameters are established, a more precise analysis of near-field mineralogy and its influence on the geochemical processes involved in radionuclide retardation should be completed.

Far-field mineralogy is an important aspect of the repository, since emphasis is given in performance assessment to the ability of the host rock in the far-field to retard radionuclides that may be released from the waste package and migrate in groundwater from the near-field. The far-field minerals establish conditions such as pH, Eh, etc., which yield favorable geochemical parameters for retardation of radionuclides through sorption. The basalt primary, secondary, and accessory minerals have been well established in most cases (MEYERS 1981); (NOONAN 1980); (SCR 1982). The primary minerals are pyroxene, plagioclase, magnetite, olivine, and interstitial glass. Major secondary minerals formed by subsequent alteration include smectite clay, zeolite, and silica. A variety of accessory minerals are present, primarily in fractures and vugs. With the

exception of the mineral couple responsible for establishing the far-field Eh, little uncertainty remains in the identification of the far-field minerals in the Columbia River basalt flows.

Sorption of radionuclides from groundwater onto near-field and far-field components is an important geochemical process which may substantially retard the radionuclide migration rate, compared to the groundwater migration rate. Radionuclides may be adsorbed on host rock and/or backfill primary, secondary, and/or accessory minerals. Backfill may be crushed basalt and thus display sorption properties similar to the host rock. Considerable information describing sorption on basalt and secondary minerals has been developed (AMES 1980); (BARNEY 1981); (BENSON 1980); (SALTER 1981a); (SALTER 1981b); (SCR 1982). The sorption value (distribution coefficient) is primarily dependent upon the specific rock minerals, the groundwater composition (ions, Eh, and pH), temperature, and radionuclide speciation. In general, high distribution coefficients were observed for many radionuclides which may exist as cations, including most actinide species, particularly under repository conditions. However, radionuclides which may be present as anions showed poor sorption on basalt minerals. Most of the experimental work was done under oxidizing conditions, although the basalt minerals are expected to establish highly reducing conditions (SCR 1982). Thus, much of the sorption test results may be of limited application to far-field conditions and modeling, although they may be more directly related to the near-field conditions shortly after repository closure when the engineered system environment may still be oxidizing.

Many uncertainties exist which are difficult to quantify. For instance, the use of an additional component (buffer) in the backfill to selectively bind anionic radionuclides has been suggested, but its identity has not been established. The basalt secondary and accessory minerals are more prevalent in the interflow and interbed regions of the repository and may be more important to sorption and radionuclide retardation than the primary minerals, although the primary minerals are present in much greater amounts. This is important since the interflow and interbed regions are more permeable and represent potential groundwater migration pathways. Uncertainties as to the methods of representing and calculating sorption benefits for the performance assessment may have restricted the emphasis

being assigned to the sorption process. Complex sorption isotherm shapes have made computational methods difficult, and sorption-desorption disequilibrium has introduced further uncertainties. No experimental investigation of multiple speciation effects by column methods were described (SCR 1982), and thus, for actinides and fission products like technetium or selenium which frequently display more than one species in solution (i.e., do not readily reach thermodynamic equilibrium), the batch distribution coefficients may be only averages of the values for the species present. Multiple speciation effects, if undetected, could introduce substantial errors when the sorption behavior is utilized in performance assessment modeling. Sorption is a broad term and the observed values may result from several chemical reactions, such as ion exchange, chemisorption, hydrolysis precipitation, etc. These are generally unquantified in test work and sometimes are unknown. In general, extrapolation of short-time -- small-scale laboratory experimental sorption results to repository behavior over geologic times is considered difficult and contains unquantified uncertainties.

Transport of radionuclides as insoluble or colloidal material can be complex. Colloidal or finely dispersed particulates may be formed in the near-field as groundwater contacts the waste form. Filtration is the geochemical process which leads to retardation or retention of insoluble material in geologic media, while colloidal material may be retarded by sorption. Very little attention seems to have been given to colloid/particulate formation reactions, to the filtration or sorption processes for these, or to favorable or unfavorable process parameters in the Site Characterization Report (SCR 1982). The present state of knowledge of colloid/particulate migration or retardation of radionuclides in either the near-field or far-field is so incomplete that the needed information has not even been identified and, thus, no discussion of the uncertainties is possible.

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

In order to establish the radionuclide retardation to be expected in the near-field, including the backfill, many engineered system parameters and components must be defined. These include waste form and load, and backfill components. After these are finalized, the form of radionuclides which might be

released from the waste, the thermal and radiation pulse effects, and thus the expected radionuclide retardation must be quantified. Additional experiments under expected repository conditions will be necessary to verify (see SIA 3.3) radionuclide retardation in the near-field. In the far-field, additional work to define sorption values at expected far-field parameters of Eh, etc., may be needed. The entire question of colloid/particulate transport must be defined and quantified.

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

Backfill, its role in helping isolate the waste package from groundwater intrusion, and in retarding radionuclide migration from the waste package to the near-field in a groundwater-intrusion -- waste-package-failure event, is thoroughly covered in the Site Characterization Report (SCR 1982). SCR issue W.1.B, "Is a unique borehole backfill required?", and the work elements related to this issue, address plans to establish backfill requirements and to identify material(s) which will satisfy these requirements. The expected temperature and radiation regime to be experienced by backfill and the water-exclusion and radionuclide-sorption properties needed are thoroughly addressed in various work elements.

Near-field mineralogy and its influence on radionuclide retardation is not specifically addressed as an issue in the Site Characterization Report (SCR 1982). However, the use of mineralogical information and the impact of mineralogy on the parameters that control geochemical processes and radionuclide retardation are well recognized and identified in a number of work elements which are components of SCR Issues W.1, "Design," W.2, "Site Geochemistry," and W.3, "Testing and Performance Confirmation." Under SCR Issue W.2.A, "Are the geochemical and hydrologic properties of the geologic setting (in conjunction with the waste forms) sufficient to meet or exceed U.S. NRC proposed waste isolation requirements?", plans for additional petrography and mineralogy activities are identified.

Far-field mineralogy and its influence on radionuclide retardation is not specifically addressed as an issue in the Site Characterization Report (SCR 1982). However, as in the near-field, the use of mineralogical information in determining the parameters which control geochemical processes and radionuclide retardation are well recognized. Plans for resolution of SCR Issue W.2.A, "Are the geochemical and hydrologic properties of the geologic setting (in conjunction with the waste forms) sufficient to meet or exceed U.S. NRC proposed waste isolation requirements?", and SCR Issue W.2.C, "Can valid Eh measurements for the candidate repository horizons in the reference repository location be made either by potentiometric measurement or indirectly by measurement of dissolved redox couples?", address needed additional mineralogical information.

The geochemical process of sorption is not specifically addressed as an issue in the Site Characterization Report (SCR 1982); however, the need to develop additional sorption data is identified in work elements under SCR Issue W.2.A, "Are the geochemical and hydrologic properties of the geologic setting (in conjunction with the waste forms) sufficient to meet or exceed U.S. NRC proposed waste isolation requirements?", and the utilization of sorption data in modeling and analysis is treated under SCR Issue W.3.A, "Testing and Performance Confirmation." Planned work for additional sorption experiments include investigation of irreversible phenomena and the effect of multiple speciation. Confirmation of the distribution coefficients and sorption isotherms obtained in the laboratory by field migration tests may also be conducted.

Colloid/particulate formation by groundwater interaction with the waste form or dissolution/precipitation phenomena, as well as the transport of radionuclides as colloids or particulates, is only superficially treated in the Site Characterization Report (SCR 1982). It is mentioned under Work Element W.1.10.A, "Determine the formation and stability of complexes and/or colloids over expected repository near-field and far-field conditions." In the section on plans, only one sentence is devoted to colloid formation and particulate transport.

Field verification is highly desirable to establish the credibility and defensibility of the radionuclide data developed in the small-scale short-time laboratory tests. Clear plans are not presented in the SCR to show how this is to be accomplished. It could be desirable to direct more attention to field verification of radionuclide sorption behavior under realistic near-field and far-field conditions. Consideration also should be given to larger-scale field testing of waste package/backfill/groundwater conditions which could lead to colloid/particulate formation and their subsequent sorption or filtration in both the near-field and far-field environments.

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

The work elements and future plans presented in the SCR are very general and generic and, while they could encompass the needed work, considerably more detail would be required to evaluate them in terms of completeness, practicality, and likelihood of success. It would be advantageous if future revisions of the SCR could give more details of the work needed to complete the issues. Within the constraint of the limited information available, the following tentative conclusions are offered with respect to the geochemical retardation issue.

The approach to backfill development appears to be technically sound and seems likely to succeed in developing a satisfactory backfill. The greatest uncertainty which will impact on the likelihood of success lies in the area of the waste form and load. Spent fuel elements and glass or ceramic waste forms could require different backfill materials due to different behavior in the presence of groundwater. Also, the waste load has not been finalized, and this also will influence the backfill requirements and materials. The work elements in the Site Characterization Report probably cover a great enough range of possible parameters to develop either a superior backfill which can satisfy all possible situations, or a number of backfills for different situations. The issue of backfill is well treated in the Site Characterization Report.

Near-field and far-field mineralogy in the Columbia River basalts is already fairly well developed, and the limited additional testing indicated is probably adequate to meet the information needs. More detailed mineralogical data in the near-field vicinity of the planned repository is desirable. Samples for this need can only be obtained after the test shaft is drilled into the Umtanum flow. The issue of near-field mineralogical information and its use in determining radionuclide migration data or predictions seems adequately covered in the Site Characterization Report.

The plans in the Site Characterization Report for development of additional sorption data seem adequate in most respects. Additional emphasis should be given to maintaining a reducing environment during the tests, as is expected in the repository.

The colloid/particulate radionuclide transport discussion in the Site Characterization Report is confused and intermixed with a general discussion of complex ions and sorption phenomena. The treatment is inadequate and the issue cannot be resolved by the given approach or plans. It is not possible to estimate when an understanding of colloid/particulate migration/retardation may be completed since a practical approach has yet to be developed.

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ISSUE NO. 3.3

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

2. Statement of the Issue:

How is the migration behavior (including solubilization and retardation) of radionuclides being validated/verified?

3. Importance of the Issue to Repository Performance

Two primary geochemical mechanisms for controlling the transport rate of radionuclides to the biosphere are the solubilization of the radionuclides (SIA 3.1) and the retardation (SIA 3.2) of the radionuclides during migration through the geosphere. The solubilization and retardation of the radionuclides are established by the geochemical conditions (e.g., pH, Eh) along the migration path and the extent to which the speciation reflects equilibrium values as opposed to the initial state (i.e., kinetics). Parameters characterizing the solubilization (e.g., solubility products) and retardation (e.g., sorption isotherms) are being measured in the laboratory or calculated and subsequently used in predicting the performance of the repository. In order for these predictions to be satisfactory, these radionuclide solubilization and sorption values must be validated/verified to show that they accurately represent or are more conservative than those that will be encountered in a waste repository.

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

60.21 Content of application

(c) The Safety Analysis Report

- (1)(ii)(F) An explanation of measures used to confirm the models used to perform the assessments required in paragraphs (A) through (D). Analyses and models that will be used to predict future conditions and changes in the geologic setting shall be supported by using such methods as field tests, in-situ tests, laboratory tests which are representative of field conditions, monitoring data, and natural analog studies.

60.122 Siting requirements

(b) Favorable conditions

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

(c) Potentially adverse conditions

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

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

Very little work has been done concerning the validation/verification of parameters related to the migration behavior of radionuclides in basalt (MOODY 1982; SCR 1982) except a limited study done at the National Reactor Testing Station in Idaho (ROBERTSON 1973; LEWIS 1982) (see Attachments 1 and 2). Furthermore, it is not currently evident what validation/verification framework is planned by the BWIP. Potential validation/verification alternatives include:

- a. in-situ measurements of migration parameters in the formation of interest and under the conditions of interest;
- b. use of a "bounding" approach to the migration parameters employed in the performance assessment based on analytical evaluation of pertinent processes and conditions;
- c. a statistical approach that correlates migration parameters measured under a variety of conditions (MUCCIANDI 1979); and/or
- d. identification of natural analogs and relating their geochemical parameters to those of the repository.

Resolution of this issue promises to be difficult in a nominally unperturbed repository geology and even more so in a repository undergoing interaction with the radioactive waste package.

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

The most immediate need is for the BWIP to identify the approach(es) to be employed for validation/verification of migration parameters and the program for their implementation. Knowledge of this overall framework is required to further specify information requirements, but the following are typical of anticipated information needs based on the validation/verification alternatives listed above:

- a. for in-situ measurements the adequacy and reproducibility of experimental methods and results must be addressed;
- b. for the bounding approach information concerning the closure aspect (have all mechanisms and interactions been accounted for) must be supplied;
- c. for a statistical approach the amount, range, and type of data that will form the basis of the correlation must be discussed; and
- d. the use of natural analogs will require that the relevance of the analog to the BWIP site be addressed.

Following this, specific validation/verification methodologies must be identified for each important geochemical mechanism or parameter to be employed.

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

The BWIP approach(es) to validation and verification of geochemical parameters related to radionuclide migration have not been described in consolidated form in the SCR (SCR 1982). Certain specific BWIP work elements (e.g., W.1.4.A, W.2.4.A, W.2.10.C, W.3.A) allude to verification/validation in the context of in-situ experiments. However, the nature of these experiments is not defined, except in the case of Eh. The SCR contains a lengthy section on in situ test facilities (Sect. 17.2), but the geochemical aspects of the repository have not been addressed here. Evaluation of practicality and likelihood of success is not possible pending identification of the validation/verification framework and specifics.

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

As noted above, the desire for validation/verification is evident in several places in the SCR. However, the planned approach(es) of BWIP to validation and verification of geochemical parameters must be regarded as incomplete at this

time since (1) the overall framework for validation/verification has not been identified in the SCR, and (2) specific validation/verification methodologies are not mentioned.

9. References:

DOE 1980. U.S. Department of Energy, Proposed Rulemaking on the Storage and Disposal of Nuclear Waste (Waste Confidence Rulemaking): Statement of Position of the U.S. Department of Energy, DOE/NE-0007

LEWIS 1982. B. D. Lewis and F. J. Goldstein, Evaluation of a Predictive Groundwater Solute-Transport Model at the Idaho National Engineering Laboratory, Idaho, PB 82-204066.

MOODY 1982. J. B. Moody, Radionuclide Migration/Retardation: Research and Development Technology Status Report ONWI-321.

MUCCIANDI 1977. A. N. Mucciandi, T. C. Johnson, and J. Saumier, Statistical Investigation of the Mechanics Controlling Radionuclide Sorption, Task 4, Third Contractor Information Meeting, PNL-SA-8571 (CONF-7910160, Vol. 1).

ROBERTSON 1973. J. Robertson and J. Barraclough, "Radioactive and Chemical Waste Transport in Groundwater at National Reactor Testing Station, Idaho: 20-Year Case History and Digital Model," Underground Waste Management and Artificial Recharge, J. Bronstein, ed., American Association of Petroleum Geologists, Tulsa, Oklahoma, 291-332.

SCR 1982. U.S. Department of Energy, Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3.

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Issue No. 3.4

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

2. Statement of the Issue:

How are the geochemical data that have been and will be gathered shown to be appropriate for use in anticipated performance assessment?

3. Importance of the Issue to Repository Performance

Performance assessment is the tool used to determine whether or not a waste repository satisfies the applicable criteria for health and safety. As used here, appropriate data relates to its compatibility and sufficiency for use in the performance assessment, which involves computer models of the groundwater hydrology and radionuclide transport and retardation mechanisms. The primary geochemical parameters required are the retardation functions, either as a constant or a concentration dependent isotherm, and the solubility of each radionuclide or a fixed initial concentration at the point of release from a waste package. Thermodynamic data on speciation and equilibrium constants, and data on sorption mechanisms, geochemical conditions and chemical reactions in all regions aid in providing the means of establishing (or bounding) the solubility and retardation parameters used in the performance assessment.

4. Importance of the Issue to Repository Performance

60.21 Content of application

(c) The Safety Analysis Report

(1)(ii)(B) Analyses to determine the degree to which each of the favorable and potentially adverse conditions, if present, has been

characterized, and the extent to which it contributes to or detracts from isolation. For the purpose . . .

- (1)(ii)(D) The effectiveness of engineered and natural barriers, including barriers that may not be themselves part of the geologic repository operations area, against the release of radioactive material to the environment. The analysis. . .
- (1)(ii)(F) An explanation of measures used to confirm the models used to perform the assessments required in paragraphs (A) through (D). Analyses and models that will be used to predict future conditions and changes in the geologic setting shall be supported by using such methods as field tests, in-situ tests, laboratory tests which are representative of field conditions, monitoring data, and natural analog studies.

60.122 Siting requirements

(b) Favorable Conditions

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

(c) Potentially adverse conditions

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

(10) Geochemical processes that would reduce sorption, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system.

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

The data requirements for existing performance assessment codes are well known. Examples of these codes or code systems are SWIFT (DILLON 1978) and NWFT/DVM (CAMPBELL 1981) developed for use by the NRC, and the WISAP consequence analysis codes (RAYMOND 1980), developed for use by DOE. Although a preliminary performance assessment of the basalt site has been made (SALTER 1982), an analysis of the appropriateness (compatibility and sufficiency) of the geochemically-based migration parameters for use in these codes have not been made for BWIP. Both retardation and solubility effects are functions of time and location, and should be determined in this manner. However, current performance assessment codes generally cannot accommodate this space and time-dependent data.

The two major mechanisms for removing or retarding the movement of radionuclides in groundwater include sorption on the contacted minerals (see SIA 3.2) and precipitation or incorporation of the radionuclides into new mineral phases, e.g., solubility constraints (see SIA 3.1). These mechanisms are highly dependent on environmental conditions such as Eh, pH, and groundwater composition.

Considerable laboratory work and some field measurements have been completed on sorption/desorption phenomena on potential repository rock in the presence of natural and simulated groundwaters. Unfortunately, the complexity of the natural environment and the wide variability of the physical and chemical properties have made direct applications of nearly all laboratory data difficult (MOODY 1982). In applications, the sorption of radionuclides is generally modeled based on the assumption that sorption reactions are linear and fully reversible. In natural systems thermodynamic reversibility is seldom attained, and even laboratory experiments are frequently not at equilibrium. In attempting to overcome some of the difficulties inherent to the application of sorption data, the Waste/Rock Interactions Technology Program (WRIT) adopted a dual

approach. The two approaches that have been pursued in concert to identify and quantify adsorption processes are: (1) an empirical one which permits rapid measurement of distribution coefficients (K_d or R_d), and (2) mechanism studies that strive to identify, differentiate, and quantify the various physicochemical processes that control nuclide adsorption. The latter approach will produce data that is more useful in applying laboratory results to the field and is in approximate agreement with the philosophy expressed in CARNAHAN 1980: "A thermodynamically rigorous approach to the modeling of chemical processes during transport can avoid the deficiencies of the 'constant K_d ' approach, and can be used to simulate precipitation/dissolution, ion exchange, surface complexation, and other chemical processes." Attainment of such an ideal goal is not practical, but a partial attainment would be most useful in giving credibility to retardation calculations. Bounding type calculations or sensitivity studies using performance assessment codes will be necessary to establish the level of sophistication of the data for the reaction mechanisms. Similar comments apply to speciation and solubility of the radionuclides, which also affects the adsorption/desorption mechanisms.

The migration of radionuclides through the BWIP geosphere will more likely involve fractured flow as opposed to flow through a porous medium (SCR 1982), and geochemical data should be generated using rock surface/water volume ratios appropriate for this flow regime. Almost all of the available information on distribution coefficients (K_d) was determined using standard methods involving intimate contact between finely ground rock and liquid. The results from these standard methods may not be applicable to fractured basalt and be nonconservative, i.e., the experimentally effective K_d is higher than that which would exist in the actual system.

In regards to the precipitation or incorporation of the radionuclides into new mineral phases, the solubility of a particular nuclide can represent an upper bound in concentration (unless colloid formation or supersaturation effects become significant) for the expected low flow rates. In the case of unexpected high flow rates (such as for serious breach scenarios), the leach rate of the waste would tend to be the controlling mechanism in determining the radionuclide

concentration (AHN 1982). (See issues involving the waste package for a discussion of leach rates.)

The solubilities of the radionuclides that are input parameters to the performance assessment codes will be both experimental and calculated. The experimental values will possess uncertainties due to the limitations involved in duplicating in-situ conditions as well as errors inherent to the experimental procedures. The calculated values will also possess uncertainties due to limitations in modeling and in the thermodynamic data base, and which can be complicated by colloid formation and complexation. In addition, the equilibrium assumption that is necessary in these complicated calculations add further to uncertainties and the question of appropriateness of the data, particularly in the case of flow through the fractured and jointed basalt.

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

Based on the previous comments, it would appear that the appropriateness of the geochemical data generated in the past is questionable. Additionally, the type of geochemical information that should (or should not) be obtained in the future must be tailored to meet the needs of existing and anticipated performance assessment tools. Consequently, the assumptions and limitations of the speciation and transport models anticipated for use in performance assessment should be evaluated with respect to types of data available and potentially available that are needed for effective exercise of the models selected.

The ultimate judge in the appropriateness of the geochemical data is the tory experiments, in-situ experiments, and other field tests (see Issue 3.3).

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

Satisfying the information needs for this issue involves many geochemical parameters and many work elements outlined in the SCR. The work elements most pertinent to this issue are listed below.

Work Element W.1.4.A Determine the projected solubilities, kinetic behavior, and distribution for key nuclides which might be released from the waste package (see attached material from the SCR for details).

Work Element W.1.10.A Determine the formation and stability of radionuclide complexes and/or colloids over expected repository near-field and far-field conditions (see attached material from the SCR for details).

Work Element W.1.12.A Determine the extent to which the interaction between the canister materials, waste form, backfill, and host rock in a saturated environment results in retardation of radionuclides (see attached material from the SCR for details).

Work Element 2.4.A Demonstrate that geochemical conditions in the near- and far-field are such that transport of radionuclides is retarded for sufficient time to satisfy waste isolation requirements (see attached material from the SCR for details).

Work Element W.2.13.D Determine to what degree the characteristics of the geologic setting complement the engineered system (see attached materials from the SCR for details).

Work Element W.3.2.A Determine the thermodynamic and kinetic arguments that can be used to extrapolate short-term (less than two years per experiment) materials test (see attached material from the SCR for details).

In addition to these specific work elements, Performance Assessment Activity 14 (Perform Postclosure Repository Performance Assessment) is pertinent to this issue. This activity will be initiated on completion of verification, validation, benchmarking, and documentation of all codes. The main elements (see attached material from the SCR for details) include:

Post Waste Emplacement Numerical Modeling

Uncertainty Analyses

Consequence Analyses

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

The planned approaches to extending and complementing the thermodynamic data base and retardation mechanism should be adequate for the purpose of judging the appropriateness of the geochemical data for use in the anticipated performance assessment. However, a specific work element for resolving this issue should be included in the plans.

9. References:

AHN 1982. T. M. Ahn et al., Nuclear Waste Management Technical Support in the Development of the Nuclear Waste Form Criteria for the NRC, NUREG/CR-2333 (BNL-NUREG-51458).

CAMPBELL 1981. J. E. Campbell, D. E. Longsine, and R. M. Cranwell, Risk Methodology for Geologic Disposal of Radioactive Waste: The NWFT/DVM Computer Code User's Manual, NUREG/CR-2081.

CARNAHAN 1982. C. L. Carnahan, "Verification and Improvement of Algorithms Used in Radionuclide Migration Models, Task 4," in: Geochemical Assessment of Nuclear Waste Isolation, LBID-429.

DILLON 1978. R. T. Dillon, R. B. Lantz, and S. B. Pahwa, Risk Methodology for Geologic Disposal of Radioactive Waste: The Sandia Waste Isolation Flow Transport (SWIFT) Model, SAND78-1267 (NUREG/CR-0424)(1978).

MOODY 1982. J. B. Moody, Radionuclide Migration/Retardation: Research and Development Technology Status Report, ONWI-321.

RAYMOND 1980. J. R. Raymond et al., Test Case Release Consequence Analysis for a Spent Fuel Repository in Bedded Salt, PNL-2782.

SALTER 1982. P. F. Salter, W. J. Anderson, and R. A. Deju, Application of Systems Analysis to Develop Engineered Systems Performance Requirements for a Hard Rock Nuclear Waste Repository, RHO-BW-SA-2110P.

SCR 1982. U.S. Department of Energy, Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3.

SERNE 1982. R. J. Serne and J. F. Relyea, The Status of Sorption-Desorption Studies Performed by the WRIT Program, PNL-3997.

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Issue No. 3.5

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

2. Statement of the Issue:

What is the mineralogy/petrology/chemistry of the backfill prior to waste emplacement?

3. Importance of the Issue to Repository Performance

Backfilling, as discussed here, refers to materials used to fill and plug shafts, tunnels, and disposal rooms. These large man-made cavities, including basalt fracturing around these cavities, represent a short pathway to the biosphere for radionuclides released from the waste package. These pathways must be blocked with engineered barriers that are essentially impervious (except for slow diffusional processes) to radionuclide migration to eliminate this short circuit to the biosphere. Backfilling mineralogy, petrology, and chemistry will directly affect the retardation of radionuclides if they are released from the waste package. A complementary role is prevention of groundwater intrusion into the repository site. Data on backfill mineralogy/petrology/chemistry are needed for input to perform assessment analyses that will be used to demonstrate regulatory compliance.

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

60.122 Siting requirements

(b) Favorable conditions

(1) The nature and rates of tectonic, hydrogeologic, geochemical, and geomorphic processes operating within the geologic setting during

the Quarternary Period would not affect or would favorably affect the ability of the geologic repository to isolate the waste.

(5) 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.

(c) Potentially adverse conditions

(10) Geochemical processes that would reduce sorption, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system.

60.140 General requirements [of the performance confirmation program]

(d) The program shall be implemented so that:

(3) It monitors and analyzes changes from the baseline condition of parameters that could affect the performance of a geologic repository.

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

An extensive engineered barrier program (SMITH 1980), which includes borehole plugging studies, is in place at BWIP with the objective of developing, testing, and demonstrating materials, equipment, and techniques for plugging the various man-made openings (boreholes, shafts, and tunnels) in and around the repository. The program, methodology, and accomplishments in regard to materials screening (including geochemical factors) and plug designs are presented. Three other publications (SMITH 1981; SMITH 1980; HODGES 1980) discuss the engineered barrier/borehole plugging program in less detail.

The results of the plugging studies indicate that a zone of construction disturbance with relatively high permeability will exist and impact on plug designs. Plans are to grout the fractured zone prior to the plug emplacement. A conceptual plug design for tunnels includes zones of concrete and mortared basalt blocks, interrupted at intervals along their length by seepage cutoff collars of clay-

sand slurry, which extends throughout the disturbed zone. The design for shafts has only zones of compacted clay-sand mixtures and concrete seepage cutoff collars. (See attached figures from the SCR (SCR 1982) showing some conceptual plug designs.) The scheme for borehole plugging included alternating zones of gravel and clay slurry containing bentonite pellets and cement grout. The recommended backfill is Na-bentonite whose principal component is the smectite clay, montmorillonite. This clay has been well characterized generically (GRIM 1962; WEAVER 1979) and it is well known that bentonite has a sorptive capacity for many chemical species and swells on hydration. The use of bentonite has been studied in Sweden for a number of years (PUSCH 1978; NERETNIEKS 1978). The use of bentonite-sand mixtures for a basalt repository was evaluated (WOOD 1981) and a 50-50 mixture of bentonite and sand or crushed basalt was recommended. Other possibilities include the use of local glaciofluvial sand. Preliminary tests (HODGES 1980) using plug models indicate that it is possible to design mixtures of candidate plug materials with permeabilities of 10^{-8} cm/sec and also form acceptable bond strengths with the host rocks.

No significant uncertainties should exist from a geochemical standpoint prior to waste emplacement. Uncertainties in the efficacy of sealing due to installation problems could occur. Uncertainties with regard to barrier effectiveness will develop with time; minimization of these uncertainties is part of the engineered barrier program.

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

The conceptual designs for plugging openings require plugs to be less permeable and to include components with generally higher sorptive capacity than the host basalt being replaced (WOOD 1981). One potential weak link is the interface between the plug and the host rock, but swelling of the clay should insure a good bond provided that geochemical reactions do not occur between the backfill and host rock and create a short-circuit flow path to the biosphere. Final decisions are required on the materials for use in the various plugs, seals, bulkheads, and backfilling. Laboratory and field tests are required to

demonstrate the efficacy of the materials used, particularly in regard to long-term stability and interactions with the host rock.

On the basis of present knowledge, it appears that potential engineering difficulties have been addressed to the exclusion of geochemical considerations.

While a preliminary list of backfill component minerals has been compiled and a selection methodology developed (SMITH 1980, Sect. 3), attention to possible long-term geochemical reactions between waste components, back-fill components, and surrounding rock has been minimal. Projection of expected geochemical reactions and the geochemical conditions expected therefrom is needed.

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

A large number of work elements are devoted to tunnel, shaft, and bore-hole sealing which implicitly include geochemical effects. The work elements more directly concerned with geochemical effects include:

- (1) Work Element R.1.19.D Select materials and develop testing techniques required to meet repository room and tunnel sealing criteria.
- (2) Work Element R.1.20.D Determine the effect of temperature, rock-mass deformation, groundwater flow, and groundwater chemistry on materials used for seals.
- (3) Work Element R.1.21.D Develop grouts and grouting techniques that ensure acceptable sealing of disturbed rock zone.
- (4) Work Element R.1.23.D

Select materials and develop testing techniques required to meet repository room and sealing criteria.

The results of the foregoing work elements and others will be the input data for Work Element R.1.25.D, which is to prepare final specifications for sealing boreholes, tunnels, shafts, and rooms.

The final specifications will be based on field test results of selected seal methods and materials tested under repository operating conditions. The test results will be compared with performance assessment tests and the specifications revised if necessary. These specifications will become the basis for the final design of sealing techniques.

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

A considerable engineering effort is to be devoted to sealing the bore-holes, tunnels, shafts, and disposal rooms for a waste repository in basalt. The individual work elements of the SCR seem to cover the geochemical aspects in general. However, the potential geochemical reactions at interfaces of the backfill or plugging materials with the host rock, which could create a potential path to the biosphere, are not discussed specifically in the SCR. Finally, work plans shown in the SCR are not sufficiently detailed to confidently predict the likelihood of success.

9. References:

GRIM 1962. R. E. Grim, Applied Clay Mineralogy, McGraw-Hill, New York.

HODGES 1980. F. N. Hodges, J. E. O'Rourke, and G. J. Anttonen, Sealing A Nuclear Waste Repository in Columbia River Basalt: Preliminary Results, RHO-BWI-SA-50.

NERETNIEKS 1978. I. Neretnieks, Transport of Oxidants and Radionuclides Through a Clay Barrier, KBS Technical Report No. 27, Swedish Nuclear Safety Project, AB Atomenergi, Stockholm, Sweden.

PUSCH 1978. R. Pusch, Highly Compacted Na Bentonite as a Buffer Substance, KBS Technical Report No. 74, Swedish Nuclear Safety Project, AB Atomenergi, Stockholm, Sweden.

SCR 1982. U.S. Department of Energy, Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3.

SMITH 1980. M. J. Smith et al., Engineered Barrier Development for a Nuclear Waste Repository in Basalt: An Integration of Current Knowledge, RHO-BWI-SI-7.

SMITH 1981. M. J. Smith, Engineered Barrier Development for a Nuclear Waste Repository in Basalt, RHO-BWI-SA-64.

SMITH 1980. M. J. Smith and S. C. McCarel, Basalt Waste Isolation Project Borehole Plugging Studies An Overview, RHO-BWI-SA-49.

WEAVER 1979. C. E. Weaver, Geothermal Alteration of Clay Minerals and Shales: Diagenesis, ONWI-21.

WOOD 1981. M. I. Wood, E. S. Patera, Jr., and W. E. Coons, Role of a Buffer Component Within an Engineered Barrier Waste Package and a Preliminary Evaluation of Bentonite as a Backfill Material, RHO-BWI-SA-80.

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Issue No. 3,6

**1. Name of Site: Basalt Waste Isolation Project (BWIP) Hanford site,
Richland, Washington**

2. Statement of the Issue:

**What is the mineralogy/petrology/chemistry of the near-field/far-field
host rock prior to waste emplacement?**

3. Importance of the Issue to Repository Performance

The host rock is the principal natural barrier in geologic waste isolation. This issue deals with the primary minerals; issue 3.7 deals with secondary minerals which form at boundaries and along flow pathways. Knowledge of the mineralogy, petrology, and chemical composition will lead to a better understanding of the genesis and the future geochemical stability of the host rock, aid in the evaluation of the effects of waste/rock interactions on radionuclide migration, and provide information for interpreting the groundwater chemistry. Porosity and permeability control groundwater movement. This information will constitute part of the input to performance assessments that will be used to demonstrate regulatory compliance.

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

60.113 Performance of particular barriers after permanent closure

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

60.122 Siting requirements

(b) Favorable conditions

- (1) The nature and rates of tectonic, hydrogeologic, geochemical, and geomorphic processes operating within the geologic setting during the Quarternary Period would not affect or would favorably affect the ability of the geologic repository to isolate the waste.
- (5) 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.

(c) Potentially adverse conditions

- (10) Geochemical processes that would reduce sorption, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system.

60.140 General requirements [of the performance confirmation program]

(d) The program shall be implemented so that:

- (3) It monitors and analyzes changes from the baseline condition of parameters that could affect the performance of a geologic repository.

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

Considerable information is available in the literature on basalts in general (BROWN 1976; YODER 1976; CARMICHAEL 1974) and the flood basalts of the Columbia River Group of the Pasco Basin (SWANSON 1979; MYERS 1979). In the latter reference, these flood basalts were identified and correlated on the basis of stratigraphic position, chemistry, paleomagnetic properties, and borehole geophysical log character which have proved useful for correlation of major units over long distances. More recent details on the lithology, stratigraphy, and some interbed characteristics of Grande Ronde Basalts are discussed in

LONG 1981a and LONG 1981b. Most of the previously discussed information has been summarized by GUZOWSKI 1981. LONG 1981c also reported stratigraphic correlations based upon 250 major element chemical analyses of samples of the Grande Ronde Basalt. [See attached material from SCR 1982 giving a brief description of the mineralogy and figures showing the stratigraphy and intraflow structure.]

NOONAN 1980 determined chemical compositions of the major silicate minerals of the Umtanum obtained from the colonnade and entablature interflow structural types and associated glass phases.

The mineralogy of core samples from five core wells was examined in detail by AMES 1980. From the data, a firm understanding of the average Hanford basalt flow primary mineralogy was obtained. A statistical study of the relationships the flow unit chemical constituents showed positive correlation between wells. An earlier study of the mineralogy and rock-water-nuclear waste interactions was made by BENSON 1979 as part of a larger program involving the development of a model simulating basalt diagenesis in the Pasco Basin.

The uncertainties connected with the mineralogy/petrology/chemistry of the bulk host rock are minimal since the core samples can be characterized in detail. The interflow and interbed zones, however, where groundwater flow is likely to be greatest, are much more difficult to characterize, and therefore are less well known. In particular, chemical properties such as Eh in water from these zones should be known. Any uncertainties resulting from insufficient sampling can be resolved in the excavation phase.

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

All the available information on this issue needs to be thoroughly correlated with any new data. This will be necessary to ensure that understanding of the petrology, mineralogy, and chemical compositions in the horizontal and vertical directions in, and from, the repository horizon (Umtanum flow or the middle Sentinel Bluffs flow) is sufficient for safety assessment purposes.

The stratigraphy and mineralogy below the Grande Ronde is not sufficiently characterized. This could be important if migration downwards of released radionuclides occurs, as suggested by GUZOWSKI 1981. In addition, more information is required to fully characterize the flow tops and interbedded minerals since these are potential paths to the biosphere.

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

The general mineralogy, petrography, and chemistry of the Grande Ronde Basalt are well known but more detailed and extensive examinations of the candidate flows (Umtanum and middle Sentinel Bluffs) and the flows above and below them are planned.

Additional information on the composition, abundance, and texture of primary and secondary phases in the candidate flows will result from taking samples from existing and planned core holes. Techniques used to obtain these data will be electron microprobe analysis, analytical scanning-transmission electron microscopy, X-ray diffraction, modal analysis (point counting), and image analysis.

Similar data are currently being collected on samples from a surface outcrop of the Umtanum flow, located at McCoy Canyon on Umtanum Ridge. The approach used to analyze primary mineral phases will be the collection of compositional data for approximately 20 samples each from the Umtanum Ridge exposure and core hole RRL-2, followed by the collection of data for approximately four samples each from additional core holes near the reference repository location.

The following information will be collected for flows above and below the candidate horizons that are penetrated by boreholes DC-2, -4, -5 (as deepened), -12, -16A, RRL-2, and +14: (1) qualitative description of intraflow structures, (2) reconnaissance petrographic data including quantitative modal analysis, and (3) mineralogic analysis of selected samples of both primary and secondary minerals.

The mineral characterization of the candidate flows is covered in Work Element S.1.6.A and the upper and lower flows in Work Element S.1.8.

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

The assessed needs for additional bore holes to support site characterization and the test plan seem adequate with a possible exception being the characterization of the interbed minerals and rocks and underlying strata. Except by implication, the various work elements do not include interbed characterization. The discussion of the interbed materials in Chapter 6 of the SCR is in general terms and no references are given. Corroboration of the data for the repository horizon, as well as additional information, can be obtained by analyses of samples taken from the initial drifts off the shafts. For completeness, a specific work element for this latter work should be included in the work breakdown structure.

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Issue No. 3.7

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

2. Statement of the Issue:

What is the mineralogy/petrology/chemistry of secondary minerals of the nearfield/farfield host rock prior to waste emplacement?

3. Importance of the Issue to Repository Performance:

The Grande Ronde basalts have a fractured/jointed structure interspersed with vugs and possess relatively porous vesicular flow tops and bottoms. These host rock openings are generally filled or lined with secondary minerals which have been derived mostly from the alteration of basalt by circulating groundwater. These joints, fractures, and porous flow regions are potential pathways for circulating ground water carrying radionuclides leached from the waste. The secondary minerals are therefore expected to be a primary sorption substitute for the retardation of radionuclides (GUZOWSKI 1981).

Understanding of the diagenesis of basalt alteration and secondary mineral formation will aid in interpreting the groundwater chemistry, and defining the sorptive properties of the host rock prior to waste emplacement. This information will be used as part of the information base from which performance assessments will be made to determine compliance with regulations.

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

60.113 Performance of particular barriers after permanent closure

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

60.122 Siting requirements

(b) Favorable conditions

(1) The nature and rates of tectonic, hydrogeologic, geochemical, and geomorphic processes operating within the geologic setting during the Quarternary Period would not affect or would favorably affect the ability of the geologic repository to isolate the waste.

(5) 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.

(c) Potentially adverse conditions

(10) Geochemical processes that would reduce sorption, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system.

60.140 General requirements [of the performance confirmation program]

(d) The program shall be implemented so that:

(3) It monitors and analyzes changes from the baseline condition of parameters that could affect the performance of a geologic repository.

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

An early review of the secondary mineral phases present at depth in the Pasco Basin was made by Benson (BENSON 1978a). He found that silica, clinoptilolite (a zeolite) and smectite clays are the most common secondary minerals. The latter two minerals will act as sorptive materials for positively charged nuclear species.

An initial study on the nature of the minerals lining vesicle and fracture surfaces was made by Benson et al. (BENSON 1978b) on samples from a single core (DC2). In a later study (BENSON 1979), using samples from five cores, determined the relative amounts, crystallization sequence, and compositions of secondary minerals found lining vesicle and fracture surfaces. Using the same five cores, Ames (AMES 1980) characterized the secondary minerals in great detail. [See attached materials (SCR 1982) giving a brief description of the mineralogy and figures showing the stratigraphy and intraflow structure.]

Teague (TEAGUE 1980) examined the mineral assemblages in two slant cores drilled off the vertical core DC2 (BENSON 1978b). Some differences were found between the slant and vertical cores which was postulated to be due to variations in the vertical distribution of samples and the fewer slant core samples studied. The data obtained by Teague and others support a preliminary conclusion that secondary mineralization is laterally continuous, and secondary mineral assemblages and morphologies in all cores are similar.

The uncertainties connected with the mineralogy/petrology/chemistry of the secondary minerals can be minimized with detailed study of core samples. Any uncertainties in the characterization of the secondary minerals in the fractures, joints, and vugs in the disposal horizon can be resolved in the excavation phase. However, present uncertainties exist for secondary minerals in flowtops and interbeds where a wider range of core sampling would be helpful.

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

The information available, along with that which is certain to be obtained when excavating into the Grande Ronde Basalts, should characterize the secondary mineralization reasonably well with the possible exception of flowtops and interbeds. Wider ranging core samples of the flowtops and interbeds along potential flow paths may be required.

The degree of uncertainty tolerable in characterizing the secondary minerals is mostly a function of the relative importance attached to radionuclide retardation by sorption, the effect on solubility, and the understanding of the evolution of diagenesis in the Grande Ronde Basalts, which involves complex mass transfer modeling (BENSON 1980). Consequently, a detailed performance assessment for a specific site seems necessary to determine the relative importance of the secondary mineralogy.

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

The general mineralogy, petrography, and chemistry of the secondary minerals in the Grande Ronde Basalt are well known, but more detailed and extensive data in the candidate flows (Umtanum and middle Sentinel Bluffs) and the flows above and below them are required (BWIP 1982).

Additional information on the composition, abundance, and texture of primary and secondary phases in the candidate flows will be determined in samples from existing and planned core holes (BWIP 1982b). Techniques used to obtain these data will be electron microprobe analysis, analytical scanning-transmission electron microscopy, X-ray diffraction, modal analysis (point counting), and image analysis.

Similar data are currently being collected on samples from a surface outcrop of the Umtanum flow, located at McCoy Canyon on Umtanum Ridge. The approach used

to analyze primary and secondary mineral phases will be the collection of compositional data for approximately 20 samples each from the Umtanum Ridge exposure and core hole RRL-2, followed by the collection of data for approximately four samples each from additional core holes near the reference repository location.

The following information will be collected for the flows above and below the candidate horizons that are penetrated by boreholes DC-2, -4, -5 (as deepened), -12, -16A, RRL-2, and -14: (1) qualitative description of intraflow structures, (2) reconnaissance petrographic data including quantitative modal analysis, and (3) mineralogic analysis of selected samples of both primary and secondary minerals. Particular attention is to be paid to variation in secondary minerals and abundance with depth, as this could provide important input to the variation of sorptive properties as a function of depth.

The secondary mineral characterization of the candidate flows is covered in Work Element S.1.6.A and the upper and lower flows in Work Element S.1.8.

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

The assessed needs for additional bore holes to support site characterization (BWIP 1982a) and the test plan (BWIP 1982b) seem adequate, with a possible exception being the characterization of the interbed secondary minerals and rocks. Except by implication, the various work elements do not include interbed characterization. The discussion of the interbed materials in Chapter 6 of the SCR is in general terms and no references are given. Corroboration of the data for the repository horizon, as well as additional information, can be obtained by analyses of samples taken from the initial drifts off the shafts. For completeness, a specific work element for this latter work should be included in the work break-down structure.

9. References

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Issue No. 3.8

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

2. Statement of the Issue:

What are the geochemical conditions expected under anticipated repository scenarios over time at the outer package interface with the host rock and backfill, in the near-field and in the far-field?

3. Importance of the Issue to Repository Performance

Geochemical conditions, in particular temperature, pH, Eh, 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 components of the backfill, the near-field and far-field host rock including absorption and precipitation will determine the limiting concentrations of soluble species and radionuclide retardation.

If the transport pathways involve relatively large openings such as occur in vesicular basalts or within colonnade structures, geochemical conditions leading to the formation and geochemical stability of colloids and fine particulates may become very important to the prediction of rates of transport of radionuclides.

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

60.113 Content of application

(c) The Safety Analysis Report

(1)(ii)(C) An evaluation of the performance of the proposed geologic repository for the period after permanent closure, assuming anticipated

04/07/83

1 BWIP DSCA/SIA 3.8/CROFF

processes and events, giving the rates and qualities of releases of radionuclides to the accessible environment as a function of time; and a similar evaluation which assumes the occurrence of unanticipated processes and events.

60.113 Performance of particular barriers after permanent closure

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

60.122 Siting Requirements

(b) Favorable conditions

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

(c) Potentially adverse conditions

(9) Groundwater conditions in the host rock, including chemical composition, high ionic strength or ranges of Eh-pH, that could affect the solubility of the waste form or chemical reactivity of the engineered barrier system so as to increase the difficulty of designing the engineered barrier system to meet the performance objectives of Sects. 60.112 and 60.113.

(10) Geochemical processes that would reduce sorption, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system.

60.135 Requirements for the waste package and its components

(a)(1) Packages for HLW shall be designed so that the in-situ chemical, physical, and nuclear properties of the waste package and its

interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting.

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

Information available thus far on repository geochemical conditions is derived from three sources: (1) analyses of groundwater from wells in Grande Ronde basalt adjacent to the reference repository area (GEPHART 1979), (2) theoretical calculations based on the mineralogy (e.g., AMES 1980; TEAGUE 1980) of the Grande Ronde basalt (SMITH 1980; JACOBS 1981, SCR 1982, Sec. 11.4), and (3) results of hydrothermal experiments with crushed Grande Ronde basalt (BARNES 1979; WOOD 1982). Ambient temperatures in the reference repository horizons in the Grande Ronde have been estimated to range from 51 to 58±C with the maximum temperature during the thermal period projected not to exceed 300±C. Groundwater pH is hypothesized to be controlled by the most reactive basalt component -- glass and the in-situ values are pH = 9.5 ± 0.5. Increased temperature and pressure will cause lowering of pH (to pH \geq 6) due to increased solubility of silicic acid (BARNES 1979; SCR 1982, Sec. 11.4). Measured Eh values in Grande Ronde basalt groundwater range from -0.22 to +0.21 but are considered imprecise with currently available instrumentation. Thermodynamic calculations, based on the assumption that iron-bearing minerals in the host rock control redox potential, yield predicted Eh values near -0.45 volts. Uncertainty concerning both measured and calculated Eh values currently constitutes a major obstacle to prediction of repository performance. Critical ligands in groundwater from Grande Ronde basalt are fluoride and carbonate-bicarbonate species because of their potential to form soluble complexes with actinides and increase the mobility of Pu, for example (CLEVELAND 1982). Geochemical conditions have been summarized in SMITH 1980. An excerpt from the BWIP SCR, which provides a succinct summary of the current state of knowledge, is attached.

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

Geochemical conditions of the backfill are, strictly speaking, unknown until the backfill is selected. If, as is probable, crushed basalt from the site and

bentonite are used, definition of backfill initial conditions could be straightforward. The nature of changes in conditions and their persistence following closure, brought about by waste disposal activities such as excavation, and waste and backfill emplacement need to be specified, especially changes which may alter radionuclide mobility. The poisoning (i.e., identification of Eh controlling reactions) of the geochemical conditions and the rate of return to equilibrium after repository closure also need to be determined. Identification of conditions favorable to formation of colloids in the repository needs to be addressed.

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

BWIP plans to experimentally determine more precisely the geochemical conditions (ambient) present in the basalt groundwater system including collection of in-situ data from drill holes for temperature, pressure, pH and Eh. Critical Eh values will be estimated in several ways (W.2.10.C) including (1) down-hole potentiometric methods using reversible electrodes, (2) redox indicator dyes, and (3) measurement of selected redox couples (e.g., As^{3+}/As^{5+}) in groundwater. Post-closure conditions will be extrapolated from experimental data from autoclave tests (elevated temperature and pressure) using basalt and/or mineral assemblages and site groundwater (W.1.5.A). Emphasis will be placed on defining Eh-pH controlling mechanisms and the kinetics of changes from oxidizing to reducing conditions.

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

The plans for better definition of geochemical conditions both pre-emplacment and post-closure are generally adequate, but sometimes presented in a vague manner. The practicality of some of the proposed approaches to estimating Eh may be questionable. For example, it seems unlikely that attempts to make down-hole potentiometric measurements will be successful, or if such measurements are obtained, that their credibility and meaning will be established unequivocally. Indirect approaches to Eh estimation, and direct measurements at the well-head, are more likely to be successful. Plans to define Eh-pH controlling mechanisms and the kinetics of changes from oxidizing (repository operation period) to

reducing (post-closure period) conditions, although not given in much detail, represent the only practical approach to assess post-closure conditions. The experimental plans presume that the rate of return to equilibrium conditions (reducing) will be rapid enough to be detectable in laboratory hydrothermal experiments and preliminary experiments seem to confirm this (SCR 1982). Identification of conditions favorable to colloid formation is not addressed directly but may be imbedded in related work elements.

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Issue No. 3.9

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

2. Statement of the Issue:

What are the chemical reactions expected under anticipated repository scenarios over time at the outer package interface with the host rock and the backfill, in the near-field and in the far-field?

3. Importance of the Issue to Repository Performance

Repository excavation and waste emplacement will perturb the ambient chemical equilibria established over geologic time in host rock and will introduce alien materials which may not be stable over long periods in the form introduced. Chemical reactions, including dissolution, precipitation, oxidation-reduction, hydrolysis, radiolysis, complexation and sorption, among components of groundwater, host rock, backfill and outer waste package will determine the formation and removal of mobile chemical species in groundwater intruding into the waste repository. Identification of all chemical reactions of importance to radionuclide mobility along with quantification of rates of reaction represents a practical means of predicting the geochemical aspects of repository performance over long time periods.

4. Portions of 10 CFR 61 That are Directly Connected to the Issue

60.21 Content of application

(c) The Safety Analysis Report

(1)(ii)(C) An evaluation of the performance of the proposed geologic repository for the period after permanent closure, assuming anticipated processes and events, giving the rates and quantities

of releases of radionuclides to the accessible environment as a function of times; and a similar evaluation which assumes the occurrence of unanticipated processes and events.

60.113 Performance of particular barriers after permanent closure

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

60.122 Siting requirements

(b) Favorable conditions

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

(5) 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.

(c) Potentially adverse conditions

(9) Groundwater conditions in the host rock, including chemical composition, high ionic strength or ranges of Eh-pH, that could affect the solubility of the waste form or chemical reactivity of the engineered barrier system so as to increase the difficulty of designing the engineered barrier system to meet the performance objectives of Sects. 60.112 and 60.113.

(10) Geochemical processes that would reduce sorption, result in degradation of the rock strength, or adversely affect the performance of the engineered barrier system.

- (11) For disposal in the saturated zone, groundwater conditions in the host rock that are not reducing.

60.135 Requirements for the waste package and its components

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

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

The nature of important reactions within the repository are thought to depend chiefly on specific characteristics of the host basalt, particularly its secondary mineralogy, and on groundwater properties (BARNEY 1981a,b; BENSON 1979). Proximity to the waste form (thermal and radiation gradients) and the final choice of components for the engineered barrier system will also define reactions. The present state of knowledge of solubility (dissolution and precipitation) and sorption reactions relevant to BWIP are summarized in Issues 3.1, 3.2 and 3.3 and are not repeated here.

A variety of candidate reactions between host rock and groundwater have been identified which may control intensive variables such as pH and Eh known to be important in determining radionuclide mobility. For example, SMITH 1980, proposed that at elevated temperatures hydrolysis of the glassy component of Hanford basalt and precipitation of clay are the principal controls on pH. These reactions occur at different rates and have opposite effects leading to complex variation of groundwater pH with time. At low water: rock ratios (equivalent to low groundwater flow rates) simple dissociation of silicic acid appears to control pH. Hydrothermal experiments up to 300±C (BARNES 1979) confirm this hypothesis suggesting that uncertainty on this aspect is low.

Eh control is hypothesized by SMITH 1980 to derive from Fe(II)-bearing secondary minerals in the Hanford basalts which control oxygen fugacities. The predicted Eh range for a closed repository according to this model is from -0.45 to -0.55 volts depending on temperature (60 to 300±C). Much uncertainty surrounds this prediction because it is based on an assumption of a very specific mineral assemblage (quartz-fayalite-magnetite) as being redox-active. Other assemblages are also possible and would lead to different calculated Eh ranges. Actual Eh measurements, although considered imprecise, suggest more oxidizing conditions (SCR 1982). Additional uncertainty arises in considering how rapidly Eh values will return to equilibrium (or geologic control) after repository closure. Detailed reaction kinetics are lacking but results of preliminary groundwater experiments (WOOD 1982; SCR 1982) have suggested that return to strongly reducing conditions is rapid (hours to months), at least for experiments using crushed basalt (i.e., possible analog of backfill).

Radiolysis reactions in aqueous solutions yield, among other things, the long-lived molecular products H₂ and H₂O₂. Depending on conditions, oxidation potential (Eh) of the solution may either increase or remain constant. The BWIP SCR (SCR 1982) suggests that under the highly reducing environment of a sealed and decommissioned repository in basalt, a high H₂ fugacity will suppress the tendency of Eh to increase in irradiated groundwater. In the absence of experimental verification some uncertainty must be assigned to this hypothesis, especially because the reestablishment of highly reducing conditions has not been demonstrated with certainty.

Short-term hydrothermal tests (BARNES 1979) have been conducted to determine the mineral alteration phases at temperatures expected in the repository backfill and near-field. Thus far these studies have suggested that alteration phases at up to 300±C are similar to the secondary mineral assemblages present in the original basalt.

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

Identification of mineral-water reactions that control Eh in various zones of the repository represents the most important needed information. The effect of

groundwater radiolysis on Eh values also needs to be examined experimentally. The kinetics by which repository conditions (especially Eh) will return to original equilibria, or evolve to new equilibria imposed by repository construction and waste emplacement is virtually unknown but is vital information to close out this issue. It must also be confirmed that key radionuclide redox couples, e.g., Tc(VII)/Tc(IV), will be reductive (i.e., exhibit equilibrium) with the mineral redox couple controlling repository Eh. Nonequilibrium between these couples will invalidate predictions of repository performance over time which are based on Eh values derived from the mineral couple. Another sub-issue, as yet unresolved, pertains to whether accelerated dissolution of potassium from basalt backfill (due to elevated temperatures) will lead to degradation of the Na-bentonite additive proposed for use in the backfill. The concern here is that leached potassium will replace sodium in the bentonite and reduce its desirable swelling properties.

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

BWIP plans to approach the definition of Eh controlling reactions using a combination of geochemical modeling and hydrothermal experiments (W.1.5.A). The modeling will be accomplished utilizing mineralogy, water chemistry, dissolved gas and thermodynamic data to develop a model that realistically describes Eh and pH as a function of temperature. Data from hydrothermal experiments for the basalt groundwater system will be compared and contrasted with data from drill holes. The hydrothermal experiments are also expected to yield sufficient reaction rate information to allow estimation of changes in repository Eh values following repository closure. Effect of radiolysis on solution chemistry (presumably including redox conditions) will be determined using hydrothermal testing on radionuclide waste forms, packaging and host rock (W.1.3.A). Effect of accelerated potassium leaching from basalt at elevated temperature on the stability of Na-bentonite will apparently be examined under Work Element W.1.12.A but is not mentioned specifically.

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

The plans for identifying important chemical reactions under anticipated repository scenarios over time are generally adequate, although not always presented in enough detail to permit evaluation. The proposed extensive use of hydrothermal studies with the host basalt and groundwater is a reasonable approach but experimental materials and conditions need to be carefully chosen to be relevant. For example, whereas crushed basalt may be relevant for defining backfill chemical reactions, an assemblage of secondary minerals known to be major components of fracture fillings in the near-field and far-field is relevant to define reactions in these zones. Two sub-issues alluded to briefly in the BWIP SCR, effect of radiolysis on Eh values and effect of groundwater potassium concentrations on Na-bentonite stability, are not dealt with explicitly in BWIP plans but seem important enough that investigation should be assured. No plans were given which would approach the question of presumed equilibrium between radionuclide redox couples and the predominant mineral redox couple controlling Eh within various zones of the repository. Predictions of repository performance for redox sensitive radionuclides based on use of mineral couple data will not be reliable if equilibrium cannot be demonstrated (MORRIS 1966). Furthermore, there is experimental evidence (AUERBACH 1980) that equilibrium between soluble Pu(IV) and Pu(V) does not always prevail. A possible approach to this question could involve comparison of measured redox speciation for both the mineral couple and radionuclide couples as part of the hydrothermal testing program.

9. References

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