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May 6, 1985

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U.S. Nuclear Regulatory Commission  
623-SS  
Washington, D.C. 20555

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Dear Dave:

Enclosed is the progress report for the month of April 1985 for B0287, "Technical Assistance in Geochemistry," and the final draft of NUREG/CR-4186, ORNL/TM-9569, "Review and Assessment of Information on Geochemical Conditions at the Hanford, Washington, Candidate HLW Repository Site." The draft NUREG report has been peer reviewed and edited. As soon as technical comments are received from NRC, we will forward photo-ready mats for publication.

Sincerely,

Susan K. Whatley, Manager  
Repository Licensing Analysis  
and Support  
Chemical Technology Division

SKW: bek

Enclosures

- 1. Monthly Report
- 2. Draft-NUREG/CR-4186, ORNL/TM-9569

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*Attachment in  
packet # 5A*

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W/lt. dtd. 5/6/85 - 2 - 0287  
To: D. J. Brooks  
From: Susan K. Whatley SKW 5/6/85

MONTHLY PROGRESS REPORT FOR APRIL 1985

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: S. K. Whatley

PROJECT STAFF: J. G. Blencoe, G. K. Jacobs, A. D. Kelmers, and R. E. Meyer

ACTIVITY NUMBER: ORNL #41 37 54 92 4 (FIN No. B0287)/NRC #50 19 03 01

TECHNICAL HIGHLIGHTS:

Task 1 - BWIP Geochemical Technical Assistance

Internal peer review and editing were completed on the topical report "Review and Assessment of Information on Geochemical Conditions at the Hanford, Washington, Candidate HLW Repository Site."

Task 2 - NNWSI Geochemical Technical Assistance

The report Conceptual Hydrologic Model of Flow in the Unsaturated Zone, Yucca Mountain, Nevada, USGS Report 84-4345, by P. Montazer and W. E. Wilson, was evaluated in conjunction with our preparation of the topical review on matrix diffusion. This report describes a detailed conceptual model of groundwater flow in the unsaturated zone beneath the candidate repository site (the "primary repository area") at Yucca Mountain. The report is important because: 1) it describes and evaluates most of the important information that is currently available concerning the groundwater hydrology of the unsaturated zone at Yucca Mountain; 2) it presents a model of groundwater flow that is sufficiently integrated and detailed to allow important tentative conclusions to be drawn concerning groundwater travel times and the geochemistry of groundwaters beneath the Site; and 3) it appears to be the document that the DOE relied upon most heavily in developing the conceptual hydrologic model for the unsaturated zone at Yucca Mountain described in the Draft Environmental Assessment for the Yucca Mountain Site (DOE 1984).

The key elements of the model developed by Monazer and Wilson are:

1. The average annual rate of groundwater infiltration into Yucca Mountain (= average annual recharge rate to the water table beneath the mountain) is probably no greater than 4.5 mm/y. Also, the rate of groundwater infiltration into the mountain is variable both spatially and temporally, and probably occurs as periodic, moderately intense pulses.
2. A combination of dipping beds, permeability layering, and capillary-barrier effects results in significant lateral flow of groundwater within the Paintbrush nonwelded unit toward bounding "structural features." This lateral flow diverts a substantial fraction of downward percolating groundwater away from the underlying Topopah Spring unit, the current reference repository horizon. An important result of

this hypothesized pattern of groundwater flow is that rates of percolation through the Topopah Spring unit are decreased to 1 mm/y or less.

3. Limited fracture flow of groundwater may occur in the higher levels of the Topopah Spring unit; however, diffusion into the matrix probably diminishes the extent of fracture flow in the deeper parts of this unit.
4. It is likely that a substantial fraction of the groundwater that flows into the Calico Hills unit from the overlying Topopah Spring unit is diverted laterally (down-dip) until "structural features" are encountered which permit subsequent flow down to the water table. Vertical flux of groundwater through the Calico Hills unit is estimated to be less than 0.006 mm/y.
5. "Structural features" probably transmit the major fraction of percolating groundwaters at Yucca Mountain.

Three major shortcomings of the Montazer and Wilson model are evident. First, the patterns of groundwater flow through the unsaturated zone beneath Yucca Mountain that are inferred from the conceptual model developed by Montazer and Wilson are profoundly influenced by the conclusion that a large fraction of the groundwater that reaches the base of the Tiva Canyon welded unit is diverted down-dip along the contact between this unit and the underlying Paintbrush nonwelded unit. This is an extremely important aspect of the model, because if this lateral flow does indeed occur to the extent envisioned by Montazer and Wilson, then it is virtually certain that very little groundwater flows through the subjacent Topopah Spring unit. However, the assumption of lateral flow in the Paintbrush nonwelded unit is largely based on theory of capillary barriers that may strictly apply only to solid materials of uniform porosity and fracture density that are in contact along a planar surface. The rocks in the Tiva Canyon welded unit and the Paintbrush nonwelded unit certainly do not have either uniform porosities or uniform fracture densities, and the boundary between these units may also be very hummocky rather than planar. Thus, the scenario of lateral (down-dip) flow of groundwater in the Paintbrush nonwelded unit described by Montazer and Wilson is probably oversimplified and may be misleading regarding the amount of lateral flow that can reasonably be expected to occur in this unit.

Second, it is implicitly assumed (from surface geologic mapping?) that "structural features" (major faults) are scarce in the central portion of the primary repository area. Evidently, the Ghost Dance fault is the only known major "structural feature" that outcrops in this area. However, on the southeastern boundary of the primary repository area where the Topopah Spring unit is at a shallower depth than it is to the north where the proposed engineered facility is to be located, major faults are in abundance; therefore, the question arises whether it is possible that additional "major" faults in the central portion of the primary repository area remain to be discovered. (Perhaps there are "major" faults in this area that do not have obvious outcrop features or do not outcrop at all.) If it is shown eventually that the Paintbrush nonwelded unit beneath the central section of the primary repository area is in fact transected by a significant number of "major faults," then it might be difficult to deny the possibility of significant and rapid fracture flow of groundwater through this unit and the underlying Topopah Spring unit.

Finally, as noted above, Montazer and Wilson apparently use the expression "structural feature" to mean "major fault," and, therefore, it is uncertain how much deformation would have to be associated with a fracture before it would be a "major fault" according to Montazer and Wilson. The distinction is important, because Montazer and Wilson state that flow of groundwater through "fractures" is very unlikely in both the Paintbrush and Calico Hills nonwelded unit, but that flow through "structural features" in these units is the predominant mechanism of groundwater movement toward the water table beneath Yucca Mountain.

Task 3 - Salt Geochemical Technical Assistance

No activity this month.

Task 4 - Short-Term Geochemical Technical Assistance

No activity this month.

Task 5 - Project Management

As discussed earlier, the geochemistry data base is being moved from the ORLOOK system to the INQUIRE system. Although ORLOOK is a searchable computerized system that can be accessed by on-site or off-site users on a time-sharing basis, it is not an interactive system and the output must be obtained by batch requests. ORNL is in the process of transferring the data bases maintained under ORLOOK to the INQUIRE system, which is an interactive system that can also be accessed by on-site or off-site users on a time-sharing basis. In addition, the INQUIRE system is faster and has a versatile report generator. Since the software exists for transferring the data base to the new system, very little costs will be incurred in the transfer.

As requested in the NRC Project Manager's letter of March 14, 1985, we are currently placing more emphasis on evaluating the documents in the data base. We are reviewing the entire data base and assigning priorities to the documents to be reviewed. Those documents that appear to have little or no relevance to the site characterization of the proposed high-level nuclear repositories and/or to the mobility of radionuclides in geologic media under the anticipated geochemical conditions of the proposed repositories will be assigned a priority 3 rating and will not be evaluated at this time. The data base will contain a notation to that effect. A priority rating of 2 will be assigned to those documents that will receive a read-through evaluation while a priority rating of 1 will be assigned to those documents that are most relevant to the project. The priority 1 evaluations will result in a mini "technical position" on the data presented, the data collection methods used, interpretations and conclusions. In addition, the priority 1 evaluations will be reported in the monthly reports.

MEETINGS AND TRIPS: None

REPORTS AND PUBLICATIONS: None

PROBLEM AREAS: None

COST/BUDGET REPORT:

Expenditures were \$27.9K for April 1985 and \$213.3 K for FY 1985. A detailed cost/budget report will be sent under separate cover.

REVIEW AND ASSESSMENT OF INFORMATION ON GEOCHEMICAL CONDITIONS  
AT THE HANFORD, WASHINGTON, CANDIDATE HLW REPOSITORY SITE

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U.S. Nuclear Regulatory Commission  
Office of Nuclear Material Safety and Safeguards  
Washington, DC 20555  
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# Draft

## ABSTRACT

This report reviews and assesses information on the geochemical conditions of rocks and groundwaters beneath the candidate high-level radioactive waste (HLW) repository site at Hanford, Washington. Most of the technical investigations associated with determining the feasibility of constructing and operating a repository at this site are being performed and/or managed by the Basalt Waste Isolation Project (BWIP) of Rockwell Hanford Operations. Consequently, comments in this report concerning the accuracy, completeness, and relevance of available information on geochemical conditions at the Hanford Site are based principally on evaluations of BWIP documents published prior to the time of this writing (December 7, 1984).

Geochemical conditions at the Hanford Site which are discussed in detail in this report include: (1) the petrology, mineralogy, and geochemistry of candidate-repository basalt horizons; (2) ambient temperatures and pressures of candidate-repository basalt horizons; (3) chemical properties of site groundwaters; and (4) postclosure geochemical conditions (i.e., expected geochemical conditions in the disturbed zone). An evaluation of the available information on these topics indicates that much is known about ambient geochemical conditions; however, the geochemical conditions that are expected to prevail after repository closure are only poorly understood.

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## REVIEW AND ASSESSMENT OF INFORMATION ON GEOCHEMICAL CONDITIONS AT THE HANFORD, WASHINGTON, CANDIDATE HLW REPOSITORY SITE

J. G. Blencoe

### 1. EXECUTIVE SUMMARY

#### 1.1 AMBIENT GEOCHEMICAL CONDITIONS AT THE HANFORD SITE

Information on ambient geochemical conditions at the Hanford Site has been obtained principally from outcrop samples, drill cores, and various in situ and laboratory measurements of the physicochemical properties of site groundwaters. The major findings of the studies that have been performed to date include the following information concerning host-rock characteristics, temperature, pressure, and groundwater characteristics.

##### ● Host-Rock Characteristics

Rocks at the Hanford Site consist of flat-lying layered basalts that are intercalated with sedimentary interbeds and overlain by Quaternary and Recent alluvium. The basalts are fine-grained, occasionally microporphyritic, tholeiite basalts that consist principally of various amounts of the primary phases plagioclase, pyroxene, iron-oxide minerals, and glassy mesostasis. Secondary minerals in the basalts — which occur mainly in fractures, flow tops, flow bottoms, and vesicular zones — vary widely in proportion and composition from flow to flow but are typically iron-rich smectite, zeolites (usually predominantly clinoptilolite), silica minerals, calcite, and pyrite.

##### ● Temperature

Measured ranges of temperature in candidate-repository horizons (all of which occur in the Grande Ronde Basalt) are: Umtanum basalt, 56.8 to 59.5°C; McCoy Canyon basalt, 55.2 to 56.8°C; Cohasset basalt, 49.7 to 52.7°C; and Rocky Coulee basalt, 47.7 to 49.7°C.

##### ● Pressure

At the depths of candidate-repository horizons (~1000 m), lithostatic (vertical) pressure ranges from approximately 20 to 30 MPa, horizontal pressure ranges from approximately 45 to 75 MPa, and hydrostatic pressure is approximately 10 MPa.

##### ● Characteristics of Grande Ronde Groundwaters

Grande Ronde groundwaters are found to have very similar compositions in most parts of the Hanford Site. The principal chemical constituents of these groundwaters display the following dominance relationship, by weight: sodium > total silica > chloride > sulfate >

total carbonate > fluoride > potassium > calcium > magnesium. However, immediately beneath the "reference repository location" (RRL), Grande Ronde groundwaters are unusually saline and contain significant amounts of dissolved methane. (Elsewhere, nitrogen is observed to be the major dissolved gas in Grande Ronde groundwaters.) Available data also indicate that basalt influences pH and redox conditions in Grande Ronde groundwaters. Measured pHs range from 8.7 to 10.6 and have a mean value of  $9.5 \pm 0.5$  ( $1\sigma$ ). Values of Eh for Grande Ronde groundwaters, according to measurements made with platinum electrodes, vary from +0.35 to -0.2 V; however, thermodynamic calculations for basaltic mineral assemblages that are assumed to be in equilibrium with Grande Ronde groundwater yield nominal Eh values that range from -0.38 to -0.53 V.

## 1.2 EXPECTED GEOCHEMICAL CONDITIONS IN THE DISTURBED ZONE OF AN NWRB AT THE HANFORD SITE

In contrast to the abundant information that has been obtained on ambient geochemical conditions at the Hanford Site, only sketchy information is available concerning geochemical conditions that are expected to develop in the disturbed zone of a nuclear-waste repository in basalt (NWRB) constructed at the site. During the first stages of the post-closure period, it is certain that repository temperatures will start to rise (at first only near waste packages, but later throughout the engineered facility and juxtaposed host rock), and groundwater will begin to permeate the shafts, drifts, and rooms of the (now backfilled) engineered facility. Shortly thereafter, a small-scale hydrothermal system will begin to develop as groundwater comes into contact with waste packages and subsequently saturates the repository. However, the timing and details of these events are uncertain, and conclusions regarding geochemical conditions that develop and evolve during this period are, therefore, somewhat conjectural.

## 1.3 INFORMATION NEEDS AND RECOMMENDATIONS

An evaluation of the available information on geochemical conditions at the Hanford Site indicates that five principal areas of technical investigation related to repository licensing should receive further attention to ensure that acquisition of additional requisite data will proceed in an efficient and timely manner. These are:

1. The field data available at present are insufficient to unambiguously identify radionuclide-release pathways at the Hanford Site. This information is needed in order to (1) establish the geochemical conditions that prevail along these routes, (2) develop defensible conceptual models of radionuclide transport, and (3) specify radionuclide source terms at strategic points along radionuclide release pathways (e.g., at the disturbed-zone/far-field interface, and at the boundaries of the site system).

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2. DOE has yet to develop a detailed conceptual model of postclosure groundwater resaturation of an NWRB at the Hanford Site. Without such a model, DOE may not be able to demonstrate satisfactory knowledge of near-field geochemical conditions during the postclosure period, and this knowledge may be required for defensible predictions of the containment performance of engineered-system materials.
3. The data available at present are insufficient to verify the hypothesis that basalt will act as a reductant in the various geochemical environments of an NWRB at the Hanford Site. In addition to uncertainties associated with measuring/estimating redox conditions in Hanford basalts, it is possible that these conditions vary significantly with minor in situ physicochemical perturbations such as small changes in host-rock composition and/or groundwater chemistry. Similar uncertainties regarding the level and constancy of redox conditions arise in attempts to evaluate the role of basalt as a reductant in barrier materials + groundwater systems at "high temperatures" (90 to 300°C). Therefore, additional information is needed on the role of basalt as a reductant in natural and synthetic basalt/groundwater systems at 50 to 300°C.
4. Colloids and particulates are potential vehicles of radionuclide transport in the basalt/groundwater systems at the Hanford Site, but little is known about how these suspended materials might form and evolve. It is possible that physicochemical interactions between heated groundwaters and barrier materials (canister metal, packing material, backfill, and repository host rocks) will produce significant quantities of colloids and particulates and that these suspended materials may, in turn, be principal vehicles by which radionuclides are transported from the engineered facility into the far field. However, at present, it is difficult to predict the quantities of colloids and particulates that would be present in Hanford Site groundwaters during the post-containment period.
5. Theoretical arguments and experimental evidence indicate that radiation emanating from waste canisters may have profound geochemical effects on the solid materials and groundwater in and around the waste packages housed in an NWRB at the Hanford Site. However, it is uncertain that the effects of radiation are a major concern in (1) assessing the performance of waste package materials, and (2) establishing defensible source terms at the boundaries of the engineered facility. Therefore, additional research is needed to quantify the effects of radiation on geochemical conditions in and around basalt-hosted waste packages.

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## 2. INTRODUCTION

### 2.1 REGULATORY CONTEXT OF INFORMATION RELATING TO GEOCHEMICAL CONDITIONS AT THE HANFORD SITE

The Nuclear Waste Policy Act of 1982 defines the national program for disposal of civilian (commercial) high-level radioactive waste (HLW).<sup>\*</sup> This Act stipulates that the Nuclear Regulatory Commission (NRC) must issue a license before the Department of Energy (DOE) may construct an HLW repository. However, prior to being granted such a license, the DOE must demonstrate with reasonable assurance that the repository will comply with applicable NRC and Environmental Protection Agency (EPA) regulations concerning radionuclide containment and release. For example, NRC regulation 10 CFR 60.113 (NRC 1983) stipulates that, assuming anticipated processes and events, the DOE must demonstrate with reasonable assurance that: (1) containment of HLW will be substantially complete for a period of 300 to 1000 years after repository closure; and (2) after the containment period, the calculated total release rate of radionuclides from the engineered barrier system will be no greater than  $10^{-5}$  per year of the inventory calculated to be present 1000 years after repository closure. Furthermore, in proposed regulation 40 CFR 191 (EPA 1982), it is stipulated that the repository system must restrict radionuclide releases in accordance with EPA standards which specify permissible cumulative releases of radionuclides to the accessible environment over a 10,000-year period. To demonstrate compliance with these and other regulatory statutes, DOE must devise performance-assessment techniques that permit satisfactory predictions of the behavior of the repository system. Moreover, to provide reasonable assurance of the predicted performance, the technical information and conceptual models used in the performance assessments must be supported by data bases that properly document the contribution of individual processes and conditions which influence the performance of the repository system and its components.

Geochemical conditions are among the potentially favorable or adverse conditions that must be evaluated in repository performance assessments and licensing (NRC 1983) because the radionuclide-isolation performance of a repository may be partly determined by disturbed-zone and far-field geochemical conditions. For example, because waste-package performance will be influenced by the geochemical conditions that develop in the engineered facility after repository closure, it is necessary to establish values for all geochemical parameters that will have a major impact on the degradation of waste packages. The geochemical processes and conditions that are generally acknowledged to be important in waste-package

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<sup>\*</sup>HLW includes wastes from both commercial and defense sources — namely, spent fuel from nuclear reactors, wastes from nuclear weapons production, and solidified wastes from fuel reprocessing.

degradation and failure are: (1) pressure; (2) temperature; (3) groundwater composition; (4) groundwater pH and redox conditions; (5) the physicochemical properties of the crystalline and amorphous solid materials in the host rock and waste packages; (6) hydrothermal activity; (7) gamma and alpha radiation emanating from the waste form; and (8) the thermodynamics and kinetics of interactions and synergisms among the components of waste packages, groundwater, and surrounding host rock. Values for, and/or the effects of, these parameters/processes must be known within reasonable limits so that compliance with the performance objectives of containment and isolation can be demonstrated with reasonable assurance. Furthermore, in order to demonstrate compliance with EPA standards concerning cumulative radionuclide release to the accessible environment, DOE must have sufficient knowledge of ambient hydrologic and geochemical conditions at a candidate repository site to adequately identify and characterize (1) all potential radionuclide release pathways and (2) the geochemical mechanisms that will tend to limit release of radionuclides to the accessible environment. Finally, in view of the points made in the preceding discussion, it is evident that ambient geochemical conditions at a candidate repository site, as well as any changes which would be expected to occur as a result of repository construction and waste emplacement, should be well-characterized in order to provide reasonable assurance that waste-package and waste-facility designs will result in acceptable performance of the repository system.

## 2.2 PURPOSE AND SCOPE OF THIS REPORT

This document reviews and assesses published information on the geochemical conditions of rocks and groundwaters beneath the candidate HLW repository site at Hanford, Washington. Investigations of these conditions are one aspect of the multifaceted BWIP mission to (1) assess the feasibility of constructing an HLW facility in a basalt horizon beneath the Hanford Site, and (2) design and develop the facilities and technologies that are required for permanent isolation of HLW in a basalt formation should feasibility be demonstrated. Numerous BWIP reports suggest that geochemical conditions at the Hanford Site are favorable for disposal of HLW [e.g., all subregions of the repository are expected to be oxygen-deficient (reducing), and under such conditions sorption of radionuclides should be extensive and the solubilities of many radionuclides should be very low]; thus it appears likely that in attempting to demonstrate compliance with NRC and EPA regulations concerning containment and release of radionuclides from a mined HLW repository, DOE will cite ambient and postclosure geochemical conditions as a favorable feature of the Hanford Site. Should this happen, it will be important for the NRC to be in a position to assess the accuracy, completeness, and relevance of published information on these conditions. The principal purpose of this document is, therefore, to provide information assistance to the NRC in the event of such an assessment.

## 2.3 BRIEF DESCRIPTION OF THE HANFORD SITE

The Hanford Site is located in southeastern Washington, approximately 10 miles to the northwest of the city of Richland. Physiographically, the site lies within the Pasco Basin — one of several prominent topographic and structural basins in the Columbia River Plateau. The Pasco Basin is underlain by a thick sequence of Miocene volcanic rocks that are both interbedded with, and overlain by, various types of sedimentary rocks. The volcanic rocks of the region are predominantly basalt flows of the Columbia River Basalt Group. These basalts were erupted from a series of volcanic fissures located mainly to the east and southeast of the Pasco Basin. Furthermore, their high fluidity and large volume caused them to flow for long distances from their source fissures, and as a result, they inundated most of the older rocks and structures in the interior of the Columbia Plateau.

BWIP geologic studies of the Hanford Site (e.g., MYERS 1979, 1981) have provided sufficient geologic information to locate several areas on the Site where conditions appear to be suitable for constructing a mined HLW repository. Furthermore, one of these areas — a 47-km zone in the west-central part of the Site — has been identified as the leading candidate-repository site and is referred to as the "reference repository location" (RRL). Detailed geologic investigations of the RRL have shown that it is underlain by more than 50 individual Columbia River Basalt flows comprising a section greater than 1500 m thick. The deepest and most voluminous of these flows are units of the Grande Ronde Basalt, a formation that contains several flat-lying and laterally continuous basalt flows with thick and dense interiors. The Grande Ronde Basalt is overlain by the Wanapum and Saddle Mountains Basalts, which consist of approximately 20 individual basalt flows with a total maximum thickness of approximately 700 m. These flows are interbedded with contemporary clastic sediments and are overlain by up to 220 m of younger sedimentary rocks.

BWIP site-characterization activities have now progressed to the point where selection of a particular basalt flow (a reference repository horizon) is necessary to provide a proper focus for future technical investigations. At present, the Cohasset basalt is the leading candidate-repository horizon (LONG 1983). This member of the Grande Ronde Basalt lies approximately 900 m below the ground surface at the RRL and possesses an interior that appears to be sufficiently thick and dense to meet repository design and isolation requirements.

## 3. REVIEW AND ASSESSMENT OF PUBLISHED INFORMATION ON GEOCHEMICAL CONDITIONS AT THE HANFORD SITE

### 3.1 AMBIENT HOST-ROCK CHARACTERISTICS

#### 3.1.1 Petrology, Mineralogy, and Geochemistry

##### 3.1.1.1 Review

Rocks at the Hanford Site consist of flat-lying layered basalts intercalated with sedimentary interbeds that are overlain by Quaternary and Recent alluvium (MYERS 1979, 1981). There are three principal basalt formations at the Site - from oldest (deepest) to youngest (most shallow), the Grande Ronde, Wanapum, and Saddle Mountains Basalts. These formations contain large numbers of individual basalt flows, each with a more-or-less distinct "dense" interior, flow top, flow bottom, and, commonly, one or more vesicular zones. Large faults are uncommon at the Hanford Site; however, small fractures, which are primarily cooling joints, are abundant in the basalts, especially in the dense interiors of flows. Patterns of fracturing in the interiors of flows are often complex because these layers frequently contain numerous individual sublayers - entablature and colonnade zones - which were formed under somewhat different cooling conditions (entablature zones were produced during periods of comparatively rapid cooling of a flow). Therefore, fracture densities are highly variable in the flows. An important feature of essentially all fractures in the "deep" basalts at Hanford is that they are nearly completely filled with secondary minerals (LONG 1981b). Secondary minerals are also abundant in flow tops, flow bottoms, and vesicular zones.

The basalts at the Hanford Site are ordinary fine-grained, occasionally microporphyritic, tholeiite basalts. The principal solid phases in these basalts, which are present in various proportions in the flows, are plagioclase, pyroxene, iron oxide minerals, and glassy mesostasis (AMES 1980). Secondary minerals in fractures, flow tops, flow bottoms, and vesicular zones vary widely in proportion and composition from flow to flow but are typically iron-rich smectite, zeolites (usually predominantly clinoptilolite), silica minerals, calcite, and pyrite (BENSON 1982).

It has also been discovered that there is a crude zonation of secondary mineralization with depth at the Hanford Site (BENSON 1979, 1982). This zonation parallels the zonation of minerals that are found in the vesicles and fractures in "deep" basalts at the site. In these basalts, the secondary mineralization of both vesicles and fractures is dominated by clinoptilolite, smectite, and silica. Clinoptilolite occurs in 80%, smectite in 75%, quartz in 40%, cristobalite in 35%, and tridymite in 15% of these openings. However, vesicles exhibit a more complex mineralogy than fractures. Secondary minerals in fractures are nearly always



clinoptilolite, smectite, silica, illite, and pyrite. By contrast, vesicles are observed to contain minor amounts of a variety of additional secondary phases such as erionite, chabazite, analcime, vermiculite, phillipsite, gypsum, and calcite. The distribution of secondary minerals in vesicles and fractures with depth is shown in Fig. 1. The patterns of secondary mineralization in basalt flows observed in this figure are probably attributable mainly to diagenetic processes, not hydrothermal processes.

The following commentary describes some of the salient features of the patterns of distribution of important secondary minerals at the Hanford Site (see Fig. 1):

- Distribution of smectite. Smectite is observed in all drill cores and at all depths; however, it appears to be less common in core material obtained from depths greater than 600 m.
- Distribution of silica. Secondary quartz is observed in all drill cores. Opal occurs in many (but not all) drill cores and is most abundant at depths below 450 m. In several drill cores, opal is more abundant than quartz at depths from 600 to 1000 m. Over the same depth interval in other drill cores, cristobalite is the dominant silica mineral.
- Distribution of clinoptilolite. Clinoptilolite only occurs in samples obtained from depths greater than 370 m. Below this depth, it occurs in all drill cores.
- Distribution of mordenite. Mordenite is observed infrequently and only at depths greater than 880 m. The appearance of mordenite correlates fairly well with features which indicate that clinoptilolite has - or is - undergoing dissolution.
- Distribution of calcite. Calcite is found over two depth intervals: 0 to 350 m, and 975 m to core bottom.

#### 3.1.1.2 Assessment

Considerable information has been obtained on the petrology, mineralogy, and geochemistry of the rocks at the Hanford Site, but much additional data remain to be acquired. In particular, more data are needed on (1) the variations in primary mineralogy and geochemistry within, and between, the colonnade and entablature zones of individual candidate-repository basalt horizons; and (2) the nature of secondary mineralization along potential radionuclide-release pathways.

As noted above, the colonnade and entablature zones of individual basalt horizons at the Hanford Site appear to have formed under somewhat different physicochemical conditions. The modes of formation of these zones and their resulting petrologic characteristics vary considerably from flow to flow. In general, however, it appears that colonnade zones

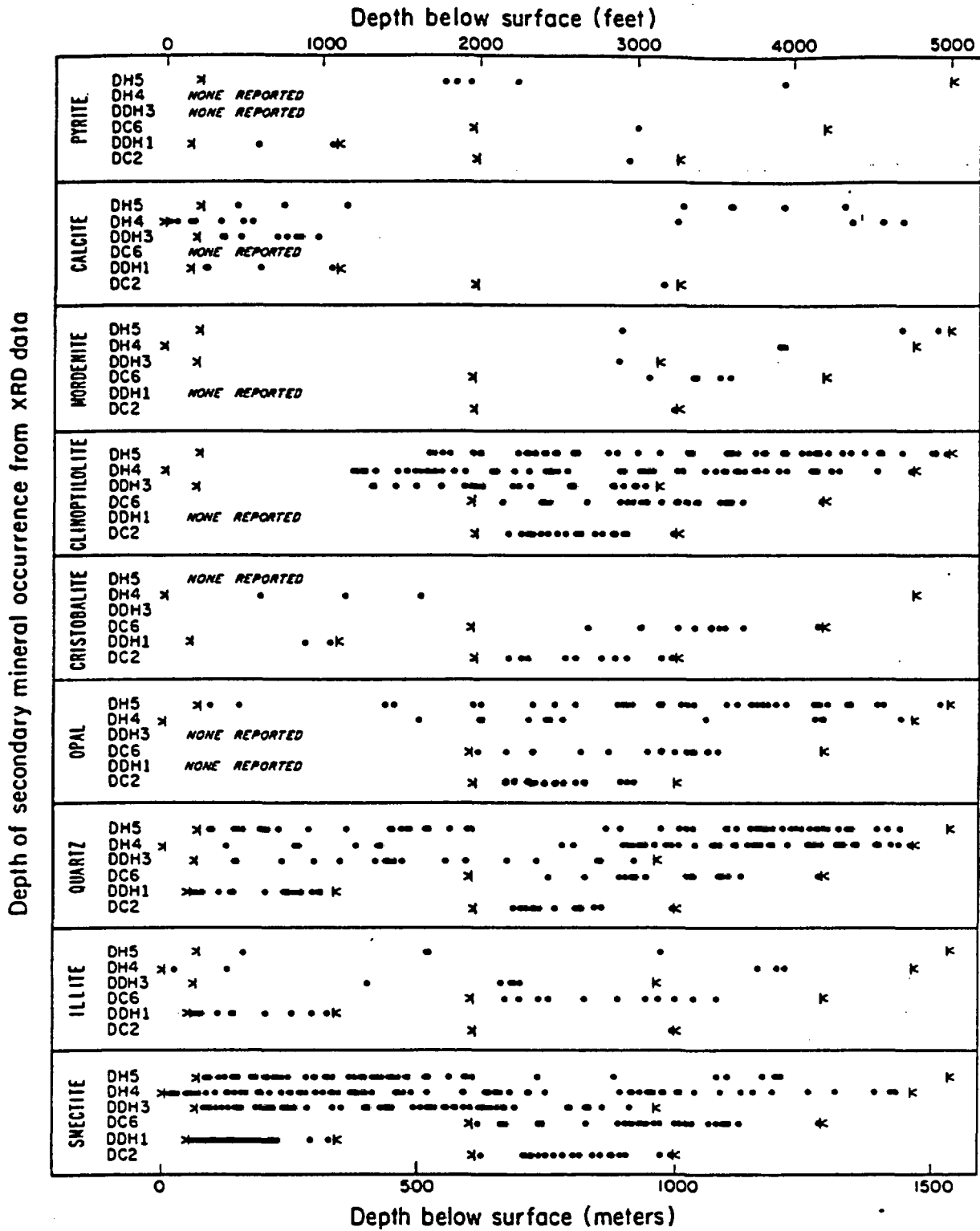


Fig. 1. Secondary mineralization versus depth for selected boreholes drilled at the Hanford Site.

Source: BENSON 1979. L. V. Benson and L. S. Teague, A Study of Rock-Water-Nuclear Waste Interactions in the Pasco Basin, Washington. Part I. Distribution and Composition of Secondary and Primary Mineral Phases in Basalts of the Pasco Basin, Washington, LBL-9677, Lawrence Berkeley Laboratory, Berkeley, Calif., 1979.

formed when rates of cooling and solidification of basalt were comparatively slow, while, by contrast, the formation of entablature zones was favored whenever rates of cooling and solidification were relatively rapid (LONG 1981a). Accordingly, the phase relations and geochemistry of the basalts in colonnade and entablature zones are expected to be somewhat different because faster rates of cooling and congealing should be reflected by (1) a fine-grained texture of the rock and a comparatively high glass/crystals ratio, and (2) a glassy mesostasis that is only slightly evolved geochemically. Feature (2) of rocks that solidified quickly — namely, basalts in entablature zones — is noteworthy because it means that the composition of the glass in a basalt (including its  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio) is partly a result of the cooling history of the rock. This conclusion, in turn, is potentially significant for repository site-characterization activities and performance-assessment analyses because Apted and Long (1982a) have proposed that local redox conditions in basalt/groundwater systems are determined largely by the amounts of  $\text{Fe}^{2+}$  that are present in groundwater due to partial dissolution of basalt glass. If this hypothesis is correct, then it is possible that redox conditions of groundwater will vary locally, depending on the composition of the glass in a basalt layer.

Data obtained by BWIP to date [summarized by Long (1983)] also indicate that, in addition to possessing differing amounts and compositions of basalt glass, rocks in colonnade and entablature zones also contain different proportions of crystalline minerals. This observation is partly attributable to the different rates of cooling in these zones, but it is also possible that the variations are partly due to different oxygen-fugacity conditions during cooling and solidification. It is important to document systematic differences between the proportions of minerals in colonnade and entablature zones because the ability of the rocks to sorb radionuclides may be influenced by the relative proportions of certain primary minerals (e.g., iron oxide and iron sulfide minerals) in the rocks.

Taken together, all of the observations and suppositions discussed above indicate that much additional research is required before the contrasting mineralogies, geochemical properties, and sorption characteristics of rocks in colonnade and entablature zones can be adequately documented and explained.

In addition to the need to obtain more data on the mineralogies and geochemical characteristics of the colonnade and entablature zones of the candidate-repository horizons at the Hanford Site, much more information should be acquired on the nature of secondary mineralization in Grande Ronde Basalt units and overlying rocks of the Wanapum and Saddle Mountains Basalts. An important observation that has already been made concerning this mineralization is that the types and amounts of secondary minerals that are found vary greatly both within an individual basalt unit and between basalt units (LONG 1983). Within individual

horizons, the greatest contrasts in secondary mineralization occur between the "dense" interiors of flows and the less dense (more permeable) flow tops, fracture zones, vesicular zones, and flow bottoms; specifically, secondary mineralization is ubiquitous in the latter zones, while the "dense" interiors of flows (where not extensively fractured) are essentially unaltered. Heterogeneity in observed secondary mineralization is even greater when different basalt units are compared with one another. For example, it has been noted by Long (1983) that, compared with the Umtanum basalt, the Cohasset flow is rich in clay minerals and deficient in zeolites, silica minerals, and pyrite. However, it is not known why these differences are observed.

Knowledge of secondary mineralization in the candidate-repository horizons at the Hanford Site, as well as some understanding of how this mineralization developed, is important because it is believed that secondary minerals will be active radionuclide sorbents in basalt/groundwater systems (SALTER 1981b). If this assumption is valid, then it will be especially important to have a thorough knowledge of the nature of secondary mineralization along potential radionuclide release pathways, which are, principally: (1) the flow tops, fracture zones, vesicular zones, and flow bottoms in candidate-repository horizons as well as in overlying basalt units; and (2) the interbeds in the Wanapum and Saddle Mountains basalts.

### 3.2 AMBIENT TEMPERATURE

#### 3.2.1 Review

Ambient subsurface temperatures at the Hanford Site have been obtained from numerous in situ measurements of the temperatures of groundwaters in boreholes. Temperature ranges for groundwaters in the Rocky Coulee, Cohasset, McCoy Canyon, and Umtanum basalt flows are listed in Table 1 (LONG 1983, TABLE I-49). When subjected to regression analysis, these temperatures, combined with those observed for groundwaters at shallower depths, yield the groundwater temperature-vs-depth equation

$$T(^{\circ}\text{C}) = 15.0 + 0.038d , \quad (1)$$

where  $d$  is depth below the surface, in meters (LONG 1983). Therefore, the geothermal gradient at the Hanford Site is  $\sim 3.8^{\circ}\text{C}$  per 100-m depth.

#### 3.2.2 Assessment

BWIP data on ambient subsurface temperatures at the Hanford Site are numerous and very consistent from one borehole to the next. Therefore, these temperatures can be regarded as known quantities in site-characterization activities and performance-assessment calculations.

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Table 1. Estimated temperatures and pressures in candidate repository horizons at the reference repository location (borehole RRL-2)<sup>a</sup>

Flow	Depth range (m) <sup>b</sup>	Temperature (°C)	Hydrostatic pressure (MPa)
Rocky Coulee	860.5–912.3 (889.0)	47.7–49.7 (48.8)	8.3–8.8 (8.6)
Cohasset	912.3–992.1 (969.6)	49.7–52.7 (51.8)	8.8–9.6 (9.4)
McCoy Canyon	1059.2–1099.4 (1081.3)	55.2–56.8 (56.1)	10.2–10.6 (10.4)
Umtanum	1099.4–1170.1 (1157.2)	56.8–59.5 (59.0)	10.6–11.3 (11.2)

<sup>a</sup>Temperature and pressure ranges listed in this table were calculated from Eqs. (1) and (2), respectively, in the text of the present report. Values in parentheses are estimated mean temperature and pressure values at the repository midline depths for each horizon encountered in borehole RRL-2.

<sup>b</sup>Depth ranges are based on the positions of upper and lower contacts of the respective horizons encountered in borehole RRL-2. Depth values in parentheses are depths to repository midlines.

Source: LONG 1983. P. E. Long, Ed., Repository Horizon Identification Report: Vol. 1, Technical Data on Candidate Repository Horizons, RHO-BW-ST-28 P, Table I-49, Rockwell Hanford Operations, Richland, Wash., 1983.

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### 3.3 AMBIENT PRESSURE

#### 3.3.1 Review

There are three principal types of pressure in the Earth's crust: vertical rock pressure (lithostatic pressure), horizontal rock pressure ("tectonic overpressure"), and hydrostatic pressure. Specifically, at any given point beneath the Earth's surface, lithostatic pressure is the load produced by the weight of superjacent rocks, horizontal pressure is the (normally) compressive stress imposed by tectonic "squeezing" of the Earth's crust, and hydrostatic pressure is the pressure generated by the weight of overlying, interconnected groundwater. Lithostatic pressure is expected to be between 20 and 30 MPa (APPS 1982) at a depth of 1000 m, which is approximately the depth at which an HLW facility would be constructed at the Hanford Site. By contrast, hydrostatic pressure at this depth would be approximately 10 MPa (see Table 1). When data on hydrostatic pressure-vs-depth at the Hanford Site are subjected to regression analysis, the result is the equation

$$P(\text{MPa}) = 0.063 + 0.0096d , \quad (2)$$

where  $d$  is depth below the surface, in meters (LONG 1983).

In situ measurements of horizontal stress at the Hanford Site have been made by the hydraulic fracturing method, a technique in which hydraulic pressure is applied to a short section of borehole until a rupture of the borehole wall occurs. Hydraulic pressure obtained by this technique permits calculations of the magnitudes of in situ stress using (1) theoretical borehole stress concentrations, and (2) various additional information concerning borehole rupture strength.

Recently, hydraulic fracturing tests were performed at 23 intervals along borehole RRL-2 where it intersected the Cohasset flow, Grande Ronde Basalt flow 7, and the Umtanum flow (LONG 1983). Results of these tests indicate that the ratio of  $\sigma_{Hmax}$  to  $\sigma_v$  (i.e., the ratio of horizontal to vertical stress) is  $\sim 2.5$  for the Cohasset flow and  $\sim 2.2$  for the Umtanum flow. (These values probably do not represent significant differences between the two flows because measurements of  $\sigma_{Hmax}/\sigma_v$  for the Umtanum flow in other boreholes range from  $\sim 2.1$  to 2.7.) Thus, because  $\sigma_v$  values (lithostatic pressures) for candidate-repository horizons range from approximately 20 to 30 MPa,  $\sigma_{Hmax}$  values probably range between 45 and 75 MPa.

The relatively high horizontal/vertical stress ratios for the Cohasset and Umtanum flows are consistent with observations of other phenomena related to high in situ stress, namely, core diskings and borehole sidewall spalling. (Disking is the phenomenon in which high-strength brittle rock, such as basalt, fractures into thin disks during and after core drilling.) Disking has been observed in drill cores from boreholes RRL-2, -6 and -14 (DOE 1982). On the average, the following percentages

of core from the dense interiors of the candidate horizons are found to be disked: Rocky Coulee flow - 56%, Cohasset flow - 30%, McCoy Canyon flow - 43%, and Umtanum flow - 73%. A second indication of high in situ stress in candidate-repository horizons is side-wall spalling in boreholes. Such spalling can be detected by lowering a television camera into the borehole. It has been found that, in a given case, there is a close correlation between the locations of spalling and the intervals of core that exhibit diskings.

### 3.3.2 Assessment

Lithostatic pressure in candidate-repository horizons at the Hanford Site can be calculated, or measured, with a high degree of accuracy; therefore, this pressure can be regarded as a known quantity for the site. Likewise, BWIP data on ambient hydrostatic pressure at the Hanford Site are numerous and very consistent from one borehole to the next, ambient hydrostatic pressure can also be treated as a known quantity in site-characterization activities and performance-assessment calculations. However, horizontal pressures in candidate-repository horizons are not known quite as accurately as are lithostatic and hydrostatic pressures. Nevertheless, it is likely that reported values (45 to 75 MPa) are reasonably accurate because measurements of the "tectonic overpressures" are similar from borehole to borehole.

## 3.4 AMBIENT GROUNDWATER CHARACTERISTICS

### 3.4.1 Groundwater Composition

#### 3.4.1.1 Review

Table 2 (LONG 1983, TABLE I-39) lists ranges of concentrations of major inorganic constituents in groundwater samples obtained from permeable zones in or adjacent to the Rocky Coulee, Cohasset, McCoy Canyon, and Umtanum basalt horizons. Examination of this table reveals that solute elements/species exhibit the following dominance relationship (by weight): sodium > total silica > chloride > sulfate > total carbonates > fluoride > potassium > calcium > magnesium. Chloride plus fluoride comprise approximately 50 to 70% of the anions, with sulfate being the major component of the remaining percentage. (However, sulfate concentrations are vanishingly small in some Grande Ronde groundwaters.) The data listed in Table 2 also show that the groundwaters from the Rocky Coulee, Cohasset, McCoy Canyon, and Umtanum flows have similar compositions.

Table 3 (LONG 1983, TABLE I-42) lists ranges of concentrations of selected trace elements in groundwater samples obtained from permeable zones in or adjacent to the Rocky Coulee, Cohasset, McCoy Canyon, and Umtanum flows. These data indicate that the concentrations of trace elements in groundwaters are similar for the four basalt horizons. The most abundant trace elements are aluminum, boron, and iron.

Table 2. Range of concentration of major inorganic constituents and hydrochemical parameters of groundwaters from all boreholes penetrating the candidate repository horizons

Chemical constituent	Range (mg/L)			
	Rocky Coulee	Cohasset	McCoy Canyon	Umtanum
HCO <sub>3</sub> <sup>-</sup>	61-113	65-123	51-89	42-110
CO <sub>3</sub> <sup>2-</sup>	26-28	4.1-22	6.9-17	4.1-17
Cl <sup>-</sup>	71-507	117-404	166-451	166-451
SO <sub>4</sub> <sup>2-</sup>	1.4-76	4.0-197	1.7-190	1.7-215
NO <sub>3</sub> <sup>-</sup>	0.0-0.1	<0.5	<0.5	<0.5
F <sup>-</sup>	24-27	11-22	18-42	17-47
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	12-110	27-63	51-87	27-68
OH <sup>-</sup>	1.4-0.1	0.13-0.71	0.16-0.87	0.13-0.87
Na <sup>+</sup>	161-355	163-350	259-355	259-362
K <sup>+</sup>	3.9-25	12-16	6.7-9.4	3.4-9.4
Ca <sup>2+</sup>	1.3-2.9	1.6-10.4	1.6-4.1	1.6-4.5
Mg <sup>2+</sup>	0.0-0.1	<0.10-0.17	<0.01-0.04	<0.001-0.14
H <sub>4</sub> SiO <sub>4</sub>	99-148	89-149	108-132	83-132
Total dissolved solids	587-1094	546-1124	789-1038	789-1076
Eh (V) (field)	+0.03 to -0.2	+0.01 to -0.1	+0.04 to -0.1	+0.2 to -0.2
pH (field)	8.7-9.9	9.3-9.7	9.5-9.7	9.2-9.7

Source: LONG 1983. P. E. Long, Ed., Repository Horizon Identification Report: Vol. 1, Technical Data on Candidate Repository Horizons, RHO-BW-ST-28 P, Table I-39, Rockwell Hanford Operations, Richland, Wash., 1983.



Table 3. Range of trace-element concentrations for groundwater samples from the candidate repository horizons

Element	Concentration range (mg/L)			
	Rocky Coulee	Cohasset	McCoy Canyon	Umtanum
Aluminum	0.11-0.08	0.04-0.41	<0.07-0.11	<0.07-0.14
Boron	2.60-0.59	0.65-3.5	0.76-3.4	0.76-3.4
Barium	0.004-0.005	<0.005-0.02	<0.005-0.02	<0.005-0.02
Cobalt	<0.01	<0.01	<0.01	<0.01
Chromium	0.01-0.003	<0.003-0.02	<0.003-0.01	<0.003-0.01
Copper	<0.006-0.002	<0.006	<0.002-0.009	<0.002-0.009
Iron	0.82-0.08	0.06-2.0	0.02-0.20	0.009-0.5
Manganese	0.17-0.02	0.004-0.37	<0.003-0.32	<0.02-0.31
Molybdenum	0.26-0.03	0.20-0.83	<0.03-0.91	<0.03-0.91
Nickel	<0.002	<0.02	<0.02	<0.02
Lead	0.170-0.10	<0.15	<0.10-0.11	<0.10-0.11
Zinc	0.15-0.002	<0.01-0.13	<0.002-0.20	<0.002-0.20

Source: LONG 1983. P. E. Long, Ed., Repository Horizon Identification Report: Vol. 1, Technical Data on Candidate Repository Horizons, RHO-BW-ST-28 P, Table I-42, Rockwell Hanford Operations, Richland, Wash., 1983.

Table 4 (LONG 1983, TABLE I-45) presents data on dissolved gases in Grande Ronde groundwater samples obtained from boreholes DC-6, DC-14, and RRL-2. These data indicate that nitrogen makes up 96 vol % of the total dissolved gas in groundwater samples obtained from boreholes DC-6 and DC-14, with the remaining fraction consisting principally of argon and helium. By contrast, dissolved gases in groundwater samples taken from borehole RRL-2 are >96 vol % methane, with the remaining fraction consisting principally of nitrogen.

#### 3.4.1.2 Assessment

The available data on the compositions of Hanford Site groundwaters have several apparent deficiencies. The first deficiency is, simply, that the available data are insufficient. Specifically, new and/or additional data are needed on the compositions of groundwaters that flow: (1) beneath the Grande Ronde Basalt, particularly in areas near the RRL; (2) immediately above the Grande Ronde Basalt — that is, in the permeable horizons within the Wanapum Basalt; and (3) in regions surrounding the Hanford Site RRL — that is, in the 10-km areas surrounding the RRL, particularly in the permeable horizons that are potential major radionuclide-release pathways (e.g., the Frenchman Springs and Mabton interbeds). Data on the compositions of groundwaters flowing beneath the Grande Ronde Basalt are needed because boreholes drilled at the Hanford Site RRL indicate that Grande Ronde groundwaters within the Cold Creek Syncline are enriched in sodium chloride, fluoride, and methane vis-a-vis other Grande Ronde groundwaters, as well as groundwaters in the basalts and interbeds that lie at shallower depths. The source region(s) and flow rates of these unusual groundwaters should be identified because, due to the potential effects of fluoride and methane on the complexation and transport of radionuclides, it is important to determine the quantities of fluoride- and methane-rich groundwaters that flow through the basalt horizons which are currently being considered as potential hosts for an HLW facility. It would also be useful to have additional data on the compositions of groundwaters that flow in horizons above the Grande Ronde Basalt and in rocks outside the RRL because these data are needed for estimating the solubilities and sorptive properties of radionuclides in the far field of an NWRB at the Hanford Site.

Additional apparent inadequacies of the available data on the compositions of Hanford site groundwaters include the following:

- It is possible, in certain instances, that analyses of Hanford Site groundwaters are inaccurate as a result of contamination by drilling mud. However, the extent to which the accuracy of the data has been compromised by drilling mud contamination (if, in fact, it has been compromised) remains an open question at present.
- Analyses of Grande Ronde groundwaters presented in BWIP reports examined by the author do not always clearly indicate the elements/species that were found to be "not present." A case in point is phosphate ion,  $\text{PO}_4^{3-}$ , which is a potentially important complexing

Table 4. Distribution of dissolved gas components in Grande Ronde basalt zones

Borehole	Unit	Depth below ground surface (m)	Total dissolved gas (vol %)							Methane concentration (mg/L)	
			Carbon dioxide	Argon	Oxygen	Nitrogen	Carbon monoxide	Helium	Hydrogen		Methane
DC-6	Cohassett	730-822	ND								
	McCoy Canyon flow bottom; Umtanum flow top	912-938	ND								
	Umtanum flow bottom	988-1075	0.16	1.35	0.49	97.60	<0.10	0.39	<0.10	<0.10	
	Lower Grande Ronde Basalt	1076-1166	<0.01	1.60	0.12	96.80	<0.10	0.35	0.20	0.90	
	Lower Grande Ronde Basalt	1125-1133	<0.01	1.54	0.19	96.0	<0.10	0.32	0.29	1.95	
DC-14	Rocky Coulee	646-681	<0.01	1.11	0.05	98.8	<0.1	0.01	<0.01	<0.01	
	Lower Grande Ronde Basalt	993-1023	0.86	1.10	<0.01	98.0	<0.10	<0.01	<0.01	<0.01	
	Umtanum fracture zone	1269-1321	<0.01	1.23	<0.01	96.0	<0.10	0.42	0.23	1.58	
RRL-2	Rocky Coulee	829-888	NA	NA	NA	NA	NA	NA	NA	NA	
	Cohassett	992-1000	0.04	0.04	<0.01	2.36	<0.10	<0.01	<0.01	97.6	620
	McCoy Canyon flow bottom; Umtanum flow top	1087-1152	0.04	0.03	0.14	1.69	<0.10	<0.10	0.2	97.9	702
	Umtanum fracture zone	1152-1666	<0.01	0.05	0.03	3.11	<0.10	<0.10	0.11	96.7	527

NA = not available due to use of air-lift sample-collection technique.

ND = no gas detected.

Source: LONG 1983. P. E. Long, Ed., Repository Horizon Identification Report: Vol. 1, Technical Data on Candidate Repository Horizons, RHO-BW-ST-28 P, Table I-45, Rockwell Hanford Operations, Richland, Wash., 1983.

anion in groundwaters. BWIP reports (e.g., LONG 1983) do not describe analyses for  $\text{PO}_4^{3-}$  (see Table 2), and it is uncertain whether this omission means that no appropriate analyses were performed or, instead, that these analyses were performed but no  $\text{PO}_4^{3-}$  was detected.

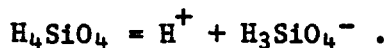
- Analyses of Grande Ronde groundwaters presented in BWIP reports (e.g., LONG 1983) are commonly presented in tables that express the concentrations of elements and/or species in terms of total ranges (see Table 2). This is unfortunate because systematic variations in groundwater composition (e.g., sympathetic or antithetic variations of a pair of elements or species) may be masked by combining data obtained from groundwaters that exhibit wide ranges in composition. In particular, it is difficult to correlate groundwater composition with host-rock chemistry when analytical data for groundwaters are reported as ranges. Detecting these correlations — if they exist — is important because they can indicate the extent to which a host rock controls the chemistry of an associated groundwater.

### 3.4.2 pH Conditions and Controls

#### 3.4.2.1 Review

Measured pH levels of groundwater samples taken from the Rocky Coulee, Cohasset, McCoy Canyon, and Umtanum flow tops vary from 8.7 to 10.6. This wide range is probably largely attributable to: (1) measurement errors, (2) in certain instances, a failure to properly correct for the effects of temperature; and (3) true variations of pH in Hanford Site groundwaters. The best estimate of the total range of pH values for Grande Ronde groundwaters (Table 5) appears to be  $9.5 \pm 0.5$  (LONG 1983, TABLE I-50).

Reactions controlling pH in Grande Ronde groundwaters have been discussed by Smith et al. (1980), Apted and Myers (1982b), and DOE (1982). The high pH values found in Grande Ronde groundwaters are consistent with groundwater isolated from the atmosphere and in contact with silicates and/or carbonates, where hydrolysis reactions result in high pH levels (KRAUSKOPF 1979). Hydrolysis of silicates appears to produce significant quantities of silicic acid,  $\text{H}_4\text{SiO}_4$ , which tends to partly dissociate in groundwater and produces hydrogen ions according to the reaction



In the pseudobinary system  $\text{H}_4\text{SiO}_4\text{-H}_2\text{O}$ , this reaction yields a solution pH of  $\sim 9.4$  at  $65^\circ\text{C}$  which is in good agreement with the measured mean pH of  $9.5 \pm 0.5$  for Grande Ronde groundwaters. This good agreement can be explained by the fact that Grande Ronde groundwaters are saturated with silica (GEPHART 1979) and contain only small quantities of other solutes which might influence groundwater pH. Therefore, it is to be expected that pHs of Grande Ronde groundwaters will be largely controlled (buffered) by the dissociation of  $\text{H}_4\text{SiO}_4$ .

Table 5. Summary Eh-pH conditions for candidate horizons and groundwater under ambient temperature conditions

pH	Eh (V)	
	Solid phases	Dissolved species
	<u>Computed results</u>	
9.0	-0.38 to -0.43	-0.42 to -0.49
10.0	-0.45 to -0.49	-0.47 to -0.54
	<u>Adopted results</u>	
9.5 ± 0.5	-0.45 ± 0.07	

Source: LONG 1983. P. E. Long, Ed., Repository Horizon Identification Report: Vol. 1, Technical Data on Candidate Repository Horizons, RHO-BW-ST-28 P, Table I-50, Rockwell Hanford Operations, Richland, Wash., 1983.

### 3.4.2.2 Assessment

The principal shortcoming of available information on pH is the failure to determine whether the presence or absence of one or more particular minerals (e.g., secondary phases such as clay minerals, zeolites, etc.) can cause pH to vary locally, or, alternatively, that pH can vary as a result of changing proportions or compositions of minerals and/or glass in the basalts and interbeds that underlie the Hanford Site. The possibility that some minerals, particularly phyllosilicates (e.g., micas and clay minerals), may have a significant effect on the pH of groundwater, especially in zones adjacent to the surfaces of the minerals, has been discussed in detail recently by Boles and Johnson (1983). These investigators suggest that micas and clay minerals can (1) possess an inherited net negative charge in the crystal framework which would attract  $H^+$  ions from solution, thereby lowering the pH of pore water (groundwater) near the surfaces of grains or crystals of the mineral; (2) adsorb  $H^+$  ions; and/or (3) exchange cations (e.g.,  $K^+$ ) for  $H^+$ , the latter two processes leading to increases in the pHs of contiguous groundwaters. This effect is particularly important whenever local rock/groundwater ratios are high because, under such conditions, both groundwater pH and groundwater composition are expected to be rock-dominated.\*

Therefore, it would be useful to investigate how pH levels of Hanford Site groundwaters are affected locally (on a mineral grain scale) by the presence of secondary phyllosilicate minerals. This effort could lead to an improved understanding of how these minerals influence the solubilities and sorptive properties of radionuclides in Hanford Site groundwaters.

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\*High rock/groundwater ratios occur where physicochemical interactions between rock and enclosed groundwater indicate that the mass of rock is much greater than that of groundwater. For example, high rock/groundwater ratios can be expected when groundwater moves only very slowly through low-permeability rocks. By contrast, a low rock/groundwater ratio implies either that: (1) the mass ratio of rock to groundwater is comparatively low; or (2) groundwater is traveling through surrounding rock at a relatively rapid rate (i.e., enclosing rocks have a high permeability), so the effective mass ratio of rock to groundwater, integrated over time, is low. The reader should note that a high rock/groundwater ratio does not require or imply any degree of equilibrium (complete, metastable, or unstable) between coexisting rock and groundwater, and, of course, the concentrations of so-called "conservative" solutes are largely unaffected by rock/groundwater ratio.

### 3.4.3 Redox Conditions and Controls

#### 3.4.3.1 Review

The Eh (redox state, or oxidation potential) of groundwaters at the Hanford Site has been measured in the field using platinum electrodes. Measured values for Grande Ronde groundwaters range from +0.35 to -0.2 V (LONG 1983). (Eh measurements made on Grande Ronde groundwaters are generally more reducing than those for groundwaters in shallower basalts.) The mechanism that controls ("buffers") redox potential in basalt/groundwater systems at the Hanford Site is inferred to be the dissolution of Fe<sup>2+</sup>-bearing basalt glass, oxidation of the resulting aqueous Fe<sup>2+</sup> ions to Fe<sup>3+</sup> ions, and (subsequently) precipitation of ferric oxides, hydroxides, or oxyhydroxides, and silica (APTED 1982a). However, Ehs measured in the field can only serve as a broad indicator of oxidizing vs reducing conditions in rock/groundwater systems because Eh determinations with a platinum electrode are frequently inaccurate due to kinetic effects at the platinum electrode surface and/or to measurement of mixed potentials from two or more couples (STUMM 1981, LINDBERG 1984). Consequently, little significance can be attached to Eh values obtained from field measurements with a platinum electrode.

A second method of estimating Eh in a basalt/groundwater system is to perform thermodynamic calculations for chemical reactions among observed solid phases and/or aqueous species that are sensitive to redox conditions (DOE 1982). Such estimates for the four candidate-repository horizons in the Grande Ronde Basalt, which are based on theoretical evaluations of geochemical interaction between solid phases and aqueous species, are quite similar (see Table 5) and collectively suggest that Eh ranges from -0.38 to -0.53 V (DOE 1982). Therefore, the weight of the evidence obtained from both Eh measurements with platinum electrodes and thermodynamic calculations indicates that Eh values in Grande Ronde groundwaters probably fall between -0.2 and -0.53 V. Owing to the great similarities in mineralogy, phase chemistry, and groundwater chemistry among the four candidate basalt flows, Long (1983) has also concluded that there are no significant differences between the Ehs of the various groundwaters in the candidate-repository horizons at the Hanford Site.

#### 3.4.3.2 Assessment

Broadly speaking, it is reasonable to conclude from available evidence that redox conditions are "reducing" in the deep basalts at the Hanford Site. However, there are significant gaps in our knowledge of the redox conditions of groundwaters in these basalts. Eh measurements performed to date are of very uncertain accuracy and significance, and BWIP has not reported the results of individual measurements. Redox conditions between -0.2 and -0.53 V probably occur — at least locally — at the depths of the candidate-repository horizons (~1000 m) at the RRL; however, in view of the results obtained by Lindberg and Runnells (1984), it seems unlikely that there is a single "master" Eh for basalt/groundwater systems

at these depths. A failure to achieve and maintain redox equilibrium in the deep basalt/groundwater systems at the Hanford Site (if and when it is demonstrated) would be reasonably attributed to sluggish kinetics of the reactions that must proceed continuously in order to establish a master Eh.

As noted above Apted and Long (1982a) have suggested that the redox conditions of Hanford Site groundwaters are controlled by  $Fe^{2+}$  dissolved from glass in Hanford Site basalts. However, this proposition is only an hypothesis, and it remains to be demonstrated that other iron-bearing minerals in Hanford Site basalts have only a negligible effect on redox conditions. It is also possible that uncertainties regarding the characteristics and spatial distribution of glass in the deep basalts at the RRL will preclude meaningful applications of the Apted and Long theory. For example, variations in the quantities of glass, as well as the proportions of different types of glass, that occur in the deep basalts at the RRL are not yet well known; nor is it known what concentrations of  $Fe^{2+}$  are typical for glasses in these basalts. Furthermore, it is uncertain how well poised redox conditions are, given the fact that deep groundwater flow paths at the RRL are mainly along fractures, flow tops, and flow bottoms. Are the redox conditions of groundwaters migrating along fractures, flow tops, and flow bottoms actually controlled by basalt glass in nearby basalt, or do secondary minerals exert the greatest control in this situation? Also, what about the redox conditions of groundwaters in interbeds at shallower depths? Are these groundwaters able to "communicate" chemically with the glass in nearby basalt so that the dissolution of basalt glass controls redox conditions, or are iron-bearing minerals in the interbeds controlling redox conditions? It seems at least possible that redox conditions can vary significantly both within and between the basalt flows and interbeds beneath the Hanford Site.

### 3.5 EXPECTED GEOCHEMICAL CONDITIONS IN THE DISTURBED ZONE

#### 3.5.1 Anticipated Postclosure Events and Processes in an NWRB at the Hanford Site

While site-characterization studies focus on ambient geochemical conditions at a candidate-repository site, analyses of waste-package performance and the development of conceptual models of radionuclide transport in the near field require information on expected geochemical conditions in the disturbed zone of the repository. This section addresses the latter geochemical conditions, which are discussed in the following order: (1) temperature; (2) pressure; (3) groundwater composition, pH, and redox conditions; (4) geochemical effects of alteration/corrosion of waste package materials, backfill, and repository host rocks; and (5) geochemical effects of radiation. Furthermore, the discussions in this section are presented in the context of a generalized model for the evolution of an NWRB at the Hanford Site. This model is based on "anticipated processes and events" in such a repository, as opposed to a model which includes one or more unanticipated processes or events ("accident scenarios"). It is emphasized that this model has been devised by the author to establish a conceptual framework for discussions of expected geochemical conditions in the disturbed zone of a repository at the Hanford Site. Therefore, the



model is not derived from BWIP technical reports. On the other hand, it is the author's opinion that many aspects of the model are consistent with commentaries and opinions presented in BWIP technical reports. The principal features of the model are described in the paragraphs below.

After closure, the repository system will experience profound physicochemical changes that are attributable primarily to (1) heat liberated by decay of radioactive material in waste canisters, and (2) groundwater resaturation. The first changes to occur after closure are a gradual increase in temperature in the repository and seepage of groundwater into the back-filled rooms and drifts of the engineered facility. Most of the groundwater that approaches waste packages at this time will either be adsorbed by bentonite in the packing material or will slowly evaporate as a result of close proximity to hot waste canisters. Then, perhaps after just a few decades, complete groundwater resaturation of the repository will occur. Boiling of groundwater near waste packages is likely at this time (especially just prior to complete repository resaturation when hydrostatic pressure is only slightly above 1 atm), and, therefore, near-field hydrothermal activity (rock/"hot-groundwater" interactions) will be initiated. These conditions lead to the formation of a pervasive "disturbed zone," which is characterized, at first, principally by: (1) elevated temperatures of the groundwater, backfill, and wall rocks of the engineered facility; and (2) gradual hydrothermal alteration of waste-package materials and backfill.

Subsequent major anticipated changes in an NWRB at the Hanford Site after groundwater resaturation, listed here in chronological order, are:

- (1) increases in the temperatures of rocks and groundwater adjacent to the engineered facility, leading to expansion of the disturbed zone;
- (2) continued canister corrosion, along with additional hydrothermal alteration of backfill material and the wall rocks of the engineered facility;
- (3) crystallization of "high-temperature" secondary minerals in the backfill material within the engineered facility and in nearby host rocks;
- (4) achievement of peak "average" repository temperatures followed shortly thereafter by a cessation in the expansion of the disturbed zone;
- (5) gradual decreases in the temperatures of the barrier materials and groundwater in and around the engineered facility, perhaps accompanied by retrograde alteration of one or more secondary solid phases that crystallized prior to, or during, the time that peak temperatures were reached in the repository;
- (6) initial failure of waste canisters, followed by physicochemical degradation of exposed water, mobilization of radionuclides (via dissolution and/or formation of radionuclide-bearing colloids and particulates), and groundwater migration of radionuclides;
- (7) continued decreases in repository temperatures and additional failures of waste canisters, mobilization of radionuclides, and groundwater transport of radionuclides; and, finally, after thousands of years, (8) a return to ambient conditions.

### 3.5.2 Temperature

#### 3.5.2.1 Review

The effects of waste emplacement on temperatures in and around the waste packages in an HLW facility in basalt have been investigated by Altenhofen (1981) and WESTINGHOUSE-AESD (1982). These studies have shown that the temperature-vs-time histories of waste packages and nearby host rock are highly dependent on repository and waste-package-design parameters as well as the physical and thermal properties of the waste-package materials and host rock. After waste packages have been emplaced in a repository, heat generated by radioactive decay will first lead to increases in temperature in waste packages; then, as time passes, the escaping heat will cause temperature to rise in the surrounding host rock. It is expected that in the very near field, peak temperatures will be achieved relatively soon after emplacement of waste packages (within ~1 to 30 years). Subsequently, very-near-field temperatures will begin to decline slowly as heat continues to be conducted away from the engineered facility; also, the heat liberated by waste packages is lower at this time because the quantities of major heat-generating radionuclides (e.g.,  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ ) that remain in the waste canisters have decreased somewhat. The overall patterns of temperature vs time in the very near field of an NWRB will be determined largely by the thermal and hydrologic properties of the host basalt.

Examples of temperature-vs-time histories in and near waste packages are illustrated in Figs. 2-4 (WESTINGHOUSE-AESD 1982). These calculations were performed using a three-dimensional finite element model that accounts for the effects of radiation, natural convection, and conduction between waste-package components. It was assumed that, during the 50-year retrieval period (i.e., before packing material is placed around the waste canisters) all heat from the emplaced waste packages will be transferred by convection and radiation across the 15-cm annulus. It was assumed that, after packing material is emplaced, the heat-transfer mechanism will be conduction through the packing material. The thermal conductivity of the packing material will be partly determined by its water content and density, both of which are difficult to predict accurately for a given point in time. Therefore, the temperature-vs-time histories illustrated in Figs. 2-4 consider only the case of dry packing material. Due to its low thermal conductivity, dry backfill will lead to the highest waste-package temperatures.

Figs. 2-4 refer to waste packages emplaced horizontally in an NWRB. The three types of waste forms considered are (1) defense high-level waste (DHLW), (2) compacted spent fuel rods (SF), and (3) commercial high-level waste (CHLW). The age of both the SF and the CHLW was assumed to be "10 years out of the reactor." Examination of the figures shows that, while the shapes of the temperature-vs-time curves depend on the initial heat-generation rate of the waste form and the rate at which heat generation decreases with time, the peak waste-package temperature is reached in each case prior to installation of packing material. The approximate temperatures and times for peak waste-centerline temperatures are: DHLW, 210°C

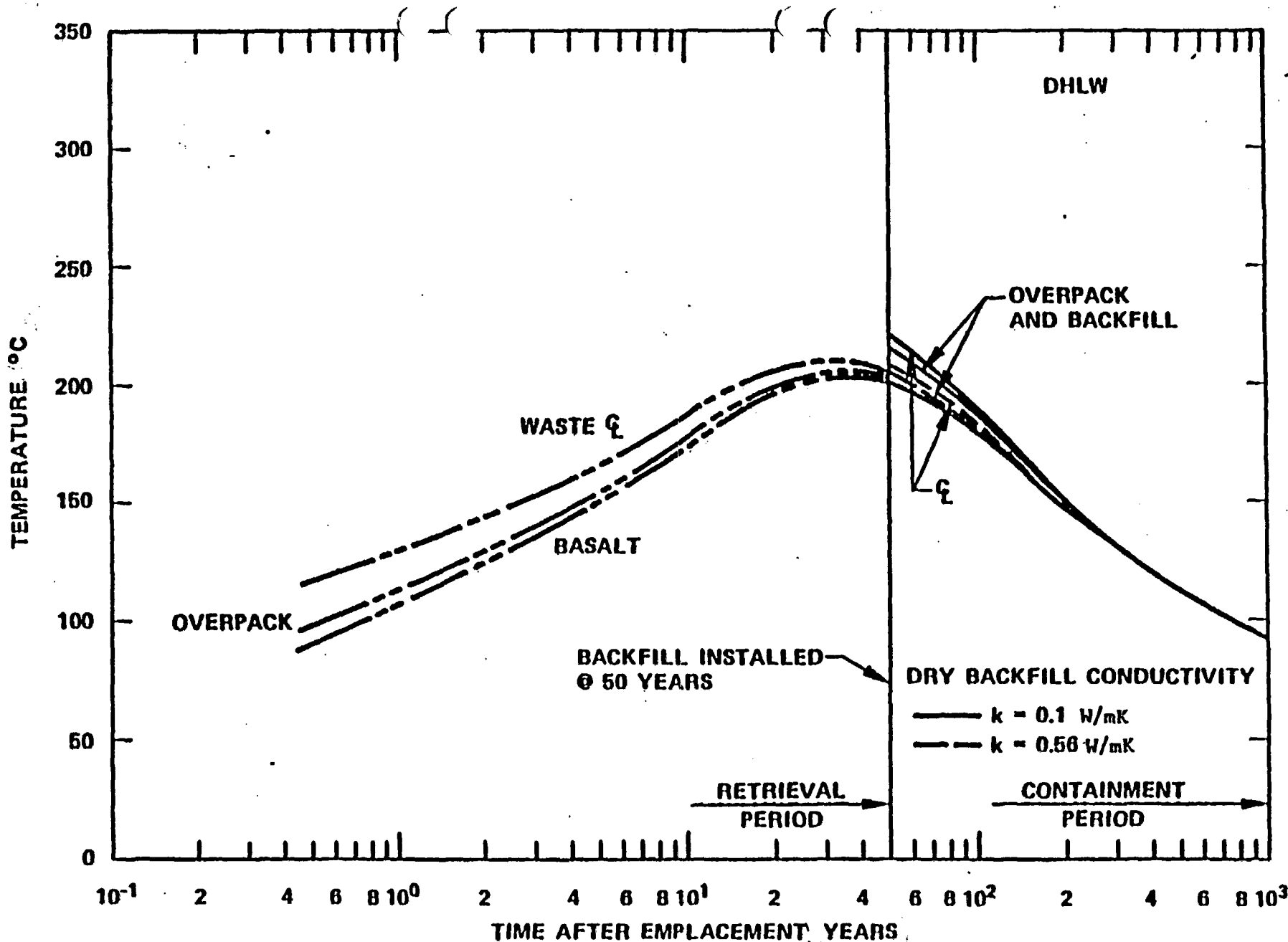


Fig. 2. Calculated temperature-vs-time histories of materials in a waste package containing defense high-level waste (DHLW). See text for explanation. Source: WESTINGHOUSE-AESD 1982. Westinghouse-AESD, Waste Package Concepts for Use in the Conceptual Design of the Nuclear Waste Repository in Basalt, RHO-BW-CR-136 P, Rockwell Hanford Operations, Richland, Wash., 1982.

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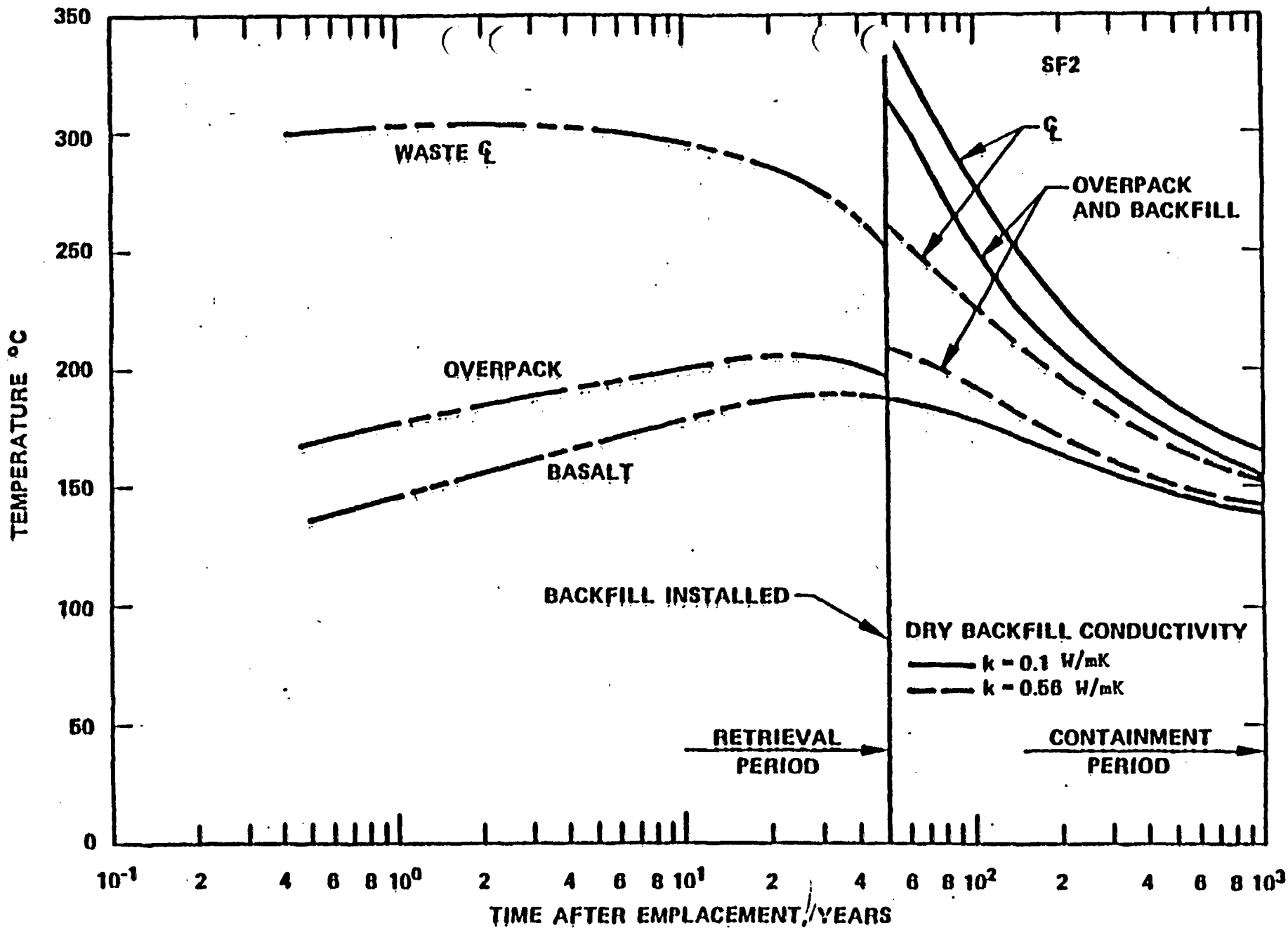


Fig. 3. Calculated temperature-vs-time histories of materials in a waste package containing compacted spent fuel rods (SF). See text for explanation. Source: WESTINGHOUSE-AESD 1982. Westinghouse-AESD, Waste Package Concepts for Use in the Conceptual Design of the Nuclear Waste Repository in Basalt, RHO-BW-CR-136 P, Rockwell Hanford Operations, Richland, Wash., 1982.

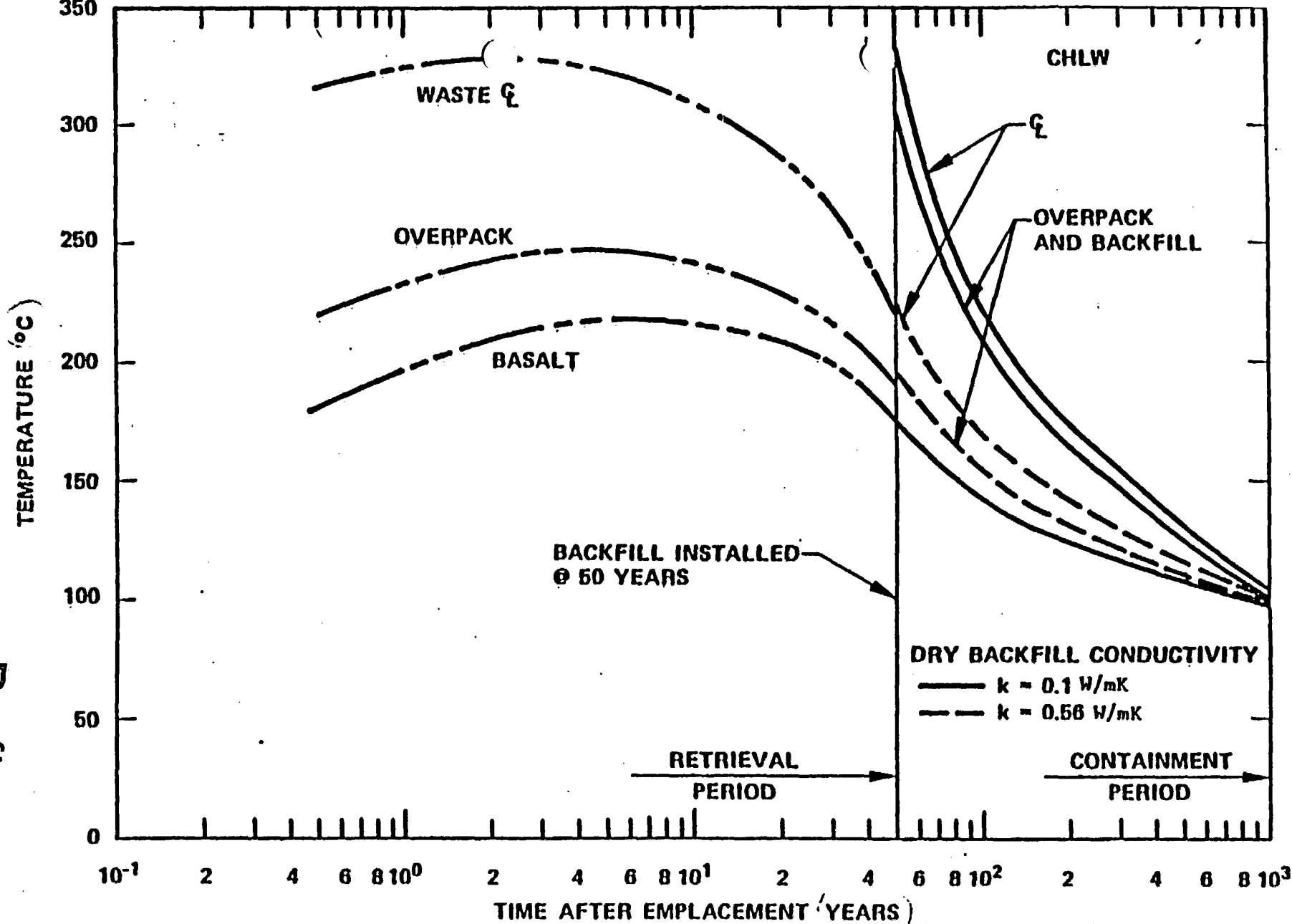


Fig. 4. Calculated temperature-vs-time histories of materials in a waste package containing commercial high-level waste (CHLW). See text for explanation. Source: WESTINGHOUSE-AESD 1982. Westinghouse-AESD, Waste Package Concepts for Use in the Conceptual Design of the Nuclear Waste Repository in Basalt, RHO-BW-CR-136 P, Rockwell Hanford Operations, Richland, Wash., 1982.

at 32 years after emplacement; SF, 303°C at 1.5 years after emplacement; and CHLW, 328°C at 2.5 years after emplacement. Immediately following installation of the packing material, the temperature of the waste-package temperatures rises due to the insulating effect of the material. The figures show two sets of curves for waste-package temperatures after installation of packing material: one set of curves based on the assumption that packing material has a thermal conductivity of 0.56 W/m·K, while the other set of curves is based on the assumption that the thermal conductivity of packing material is only 0.1 W/m·K. In the first case (i.e., with a 0.56 W/m·K thermal conductivity for packing material), there is only a modest increase in waste-package temperature immediately after emplacement of the packing material, then the thermal conductivity of the packing material will increase to an uncertain extent, and this would tend to decrease temperatures at the surface of the overpack and in the packing material. After 1000 years, regardless of the timing of groundwater contact with waste packages, waste centerline temperatures are approximately 90°C for DHLW, 160°C for SF, and 100°C for CHLW.

### 3.5.2.2 Assessment

BWIP efforts to estimate temperature increases in an NWRB during the postclosure period have been restricted to considerations of the simple scenarios of increases in temperature near waste packages. These efforts are laudable insofar as they provide good estimates of the temperatures to be expected at the surfaces of canisters and in packing material and nearby host rock, but this information is not adequate for devising a complete model of the thermal history of a mined repository. To devise such a model, it is necessary to have detailed information on (1) the thermal and hydraulic properties of engineered-barrier materials and surrounding host rock, (2) the characteristics and timing of groundwater resaturation of the engineered facility, and (3) the rates and paths of groundwater flow through the engineered facility after repository resaturation. With this information, and a knowledge of the depths and orientations of repository openings (shafts, drifts, and rooms), it would be possible to begin to develop a model of the thermal history of the repository that would properly account for the effects of circulating groundwaters which, via thermal buoyancy and convective flow would tend to transport and dissipate the heat liberated from waste canisters. It should be recognized that the development of a numerical (computer) model of groundwater resaturation of a repository and subsequent flow of groundwater through the repository after resaturation is a prerequisite for devising a valid conceptual model of waste-package-containment performance and subsequent radionuclide-isolation performance of waste packages during the postcontainment period.

### 3.5.3 Pressure

#### 3.5.3.1 Review

BWIP reports say very little about postclosure pressure in an NWRB at the Hanford Site. However, pertinent discussions in several reports (e.g., MYERS 1983) seem to be predicated on the following assumptions: (1) the engineered facility will be relatively dry and at an air pressure of ~0.1 MPa (1 atm) at the time of closure; (2) groundwater will begin to seep into

the engineered facility in significant quantities immediately after closure; and (3) hydrostatic pressure in the repository after resaturation will be ~10 MPa (i.e., approximately the same as ambient hydrostatic pressure). However, details of the changes atmospheric/hydrostatic pressure pressure that occur between the time of closure and resaturation are not discussed in detail in any BWIP report known to the author.

#### 3.5.3.2 Assessment

Changes in atmospheric/hydrostatic pressure in an NWRB at the Hanford Site that occur during the period of time from closure to repository resaturation can be estimated accurately if a detailed conceptual model of the nature and timing of repository resaturation is developed. Without such a model, however, very little can be said about atmospheric/hydrostatic pressure changes after closure except that, initially, "fluid" pressure will be ~0.1 MPa air pressure, and, after repository resaturation, pressure will be ~10 MPa hydrostatic pressure.

#### 3.5.4 Groundwater Composition, pH, and Redox Conditions

##### 3.5.4.1 Review

The relationships between temperature, composition, pH, and redox conditions of groundwater in barrier materials + groundwater systems have been investigated by BWIP staff members and contractors largely via empirical experimental studies in which barrier materials + groundwater starting materials have been allowed to react at a predetermined temperature for a sufficient period of time to determine the nature and extent of the chemical changes that occur (APTED 1982b). Modern devices for such experimentation (e.g., "rocking" autoclaves of the Dickson type) permit periodic sampling of fluid as experimentation is ongoing. This approach has the advantage that it permits changes in the composition of groundwater to be monitored as experimentation proceeds. A goal in many barrier materials + groundwater experiments performed with Dickson-type apparatus has been to achieve so-called "steady-state conditions;" specifically, experiments were allowed to continue for sufficiently long periods of time that measured properties of sampled fluid (especially the composition of fluids) were observed to be constant, or nearly so, with increasing time (MYERS 1983). The justification for this time-consuming approach to experimentation is the presumption that the resulting data will more faithfully reflect long-term barrier materials + groundwater interactions that are expected to occur in an NWRB.

Sufficient experimental data are available to firmly establish many of the salient relationships between groundwater composition and temperature in basalt + groundwater and simulated waste form + groundwater ± basalt systems (APTED 1982b, MYERS 1983). Also, reasonably accurate estimates of pH levels of the groundwaters in these systems at temperatures above 100°C have been obtained from computer codes which calculate the types and amounts of aqueous species that are present in groundwaters at elevated temperatures. However, corresponding estimates of redox conditions in the groundwaters are only qualitative at present.

Changes in the compositions of synthetic Grande Ronde groundwaters in basalt + groundwater experiments performed at a pressure of 30 MPa and temperatures of 200 and 300°C have been described in detail by Apted and Myers (1982). The principal changes are: (1) a greater than tenfold increase in dissolved silica; (2) large initial increases in the concentration of potassium, apparently followed by slow decreases in the concentration of this element; (3) a slight initial increase in the concentration of fluorine, apparently followed by significant decreases in the concentration of this element; (4) very slight and gradual decreases in the concentration of sulfate; and (5) little change in the concentrations of sodium and chlorine.

Changes in pH of the groundwaters at the temperature of experimentation could not be measured directly, so these pHs were calculated using the computer code HIPH4 (MYERS 1983). The calculations indicate that pH in basalt + groundwater systems decreases from an initial (measured) value of 9.8 at 25°C to a minimum value of nearly 8 at 240°C, and thereafter starts to increase again, reaching 8.2 at 300°C. Because neutral pH decreases steadily from 7.0 to approximately 5.5 at 300°C, it is evident that groundwater in contact with basalt is very alkaline over the temperature range 25 to 300°C. The computer calculations also indicate that, at 25°C, the pH of Grande Ronde groundwater is buffered principally by the reaction  $H_4SiO_4 = H_3SiO_4^- + H^+$ , but at higher temperatures pH is controlled mainly by the reactions  $H_2O = H^+ + OH^-$  and  $H_2CO_3 = HCO_3^- + H^+$ .

It is unfortunate, at the present time, that there exists no proven experimental or calculational method for determining redox conditions (Eh) in basalt + groundwater systems at temperatures above 100°C. Therefore, it is only possible to infer redox conditions by indirect indications. Perhaps the best indicator of reducing conditions in basalt + groundwater systems is the fact that basalt is known to have the capability of removing oxygen from groundwater at high temperatures (LANE 1984). Another indication of reducing conditions in basalt + groundwater experiments at 300°C is the apparent reduction of some sulfate to hydrogen sulfide gas (APTED 1982b). However, no evidence indicating the formation of hydrogen sulfide gas was obtained in similar experiments performed at <300°C, and this suggests that sulfate reduction may occur at only negligibly slow rates at temperatures below 300°C (OHMOTO 1982). Finally, another indication of reducing conditions in basalt + groundwater systems is the fact that recent experiments involving deoxygenated, deionized groundwater and crushed basalt indicate that an Eh of -0.4 V (measured with a platinum electrode) can be achieved at 70°C in less than 200 h (JANTZEN 1983).

#### 3.5.4.2 Assessment

A great deal of information has been obtained on the compositions, pHs, and redox conditions of groundwaters in contact with basalt at "high temperatures" (100 to 300°C). Nevertheless, additional investigations are needed to further elucidate the interactions between barrier materials (both engineered and natural) and groundwater under conditions which closely simulate those that are expected to develop in the disturbed zone of an NWRB during the postclosure period. Information obtained from these studies would help to eliminate the following important deficiencies of current data:



- BWIP hydrothermal experiments on barrier materials + groundwater systems at high temperatures are less useful than they could be because, at the present time, it is impossible to accurately measure pH and redox conditions (Eh) at high temperatures. The inability to measure pH at high temperatures is less of a problem than the inability to measure redox conditions because, apparently, pH levels of groundwaters in barrier materials + groundwater systems at high temperatures can be calculated with a fairly high degree of accuracy using the computer code HIPH4. The inability to either measure or calculate redox conditions is unfortunate, because these conditions must be known in order to accurately estimate or calculate the solubilities of radionuclides that can exist in more than one oxidation state in aqueous solutions (e.g., uranium and plutonium). (However, fortunately, quantitative information on redox conditions is not required for measuring radionuclides solubilities.) It is commendable that BWIP has initiated efforts to develop pH and Eh sensors for measuring pH and Eh directly in hydrothermal experiments performed in Dickson-type autoclaves (MYERS 1984).
- The majority of hydrothermal experiments currently being performed by BWIP — namely, closed-system "rock-water" experiments conducted in reaction vessels of the Dickson-type — do not adequately simulate the circumstances of groundwater flow through an engineered facility in an NWRB. In particular, these experiments are intrinsically incapable of revealing effects that result from groundwater flowage through a system of natural and engineered barriers. Such flowage can only be simulated closely by performing so-called "flow-through" experiments that reproduce the open-system conditions which are expected to develop in an NWRB. Preliminary flow-through experiments performed by BWIP suggest that rock/groundwater interactions under flow-through conditions are significantly different from corresponding interactions in closed-system experiments.
- In addition to an intrinsic inability to simulate the effects of open-system conditions, the "static" hydrothermal experiments performed by BWIP to date have been designed mainly to elucidate hydrothermal interactions between simulated waste forms, freshly crushed basalt, and groundwater. The use of freshly crushed basalt in these experiments is justified by BWIP (MYERS 1982) on the grounds that comminution enhances reaction rates, and increasing reaction rates makes it more likely that steady-state conditions will be achieved during experimentation. This contention is supported by a large body of direct and indirect evidence (discussion of which is outside the scope of the present commentary), and is not called into question here. Rather, the question to be considered is whether freshly crushed basalt is properly included among solid experimental starting materials that are supposed to represent the solid materials extant in an NWRB during the postcontainment period. At this time in the history of a repository — nominally at least 300 to 1000 years after repository closure — it is expected that groundwater will have already resaturated the repository and, therefore, hydrothermal interactions

between groundwater and crushed basalt (in packing material and backfill) will have been proceeding for at least several decades and perhaps several centuries. Thus, it seems likely that the basalt present in engineered barrier materials during the postcontainment period will have had ample opportunity to react with groundwater to form various secondary minerals — especially smectites and zeolites. Consequently, it is reasonable to conclude that crushed hydrothermally altered basalt is a more suitable basaltic starting material for experiments that purportedly simulate geochemical conditions in a basalt-hosted HLW facility during the postcontainment period. Use of this material would permit a determination of whether secondary minerals have important effects on geochemical conditions and radionuclide behavior in the near field of an NWRB.

- Additional, valuable information on geochemical conditions in the disturbed zone of an NWRB could be obtained by further improving simulations of near-field repository conditions. For example, to date, BWIP hydrothermal experiments have not included canister metal among the solid starting materials; therefore, the effects of this material on experimental results (and by analogy, the effects of canister metal on geochemical conditions near waste packages in an NWRB) are undetermined. Also, the potential effects of radiation on the geochemical conditions (chemistry, pH, and redox conditions) of groundwater in waste packages have yet to be determined. Finally, while it has been stated that results obtained from "static" hydrothermal experiments are essentially independent of rock/water ratio for ratios between approximately 1/1 and 1/50 (MYERS 1982), it remains to be demonstrated that corresponding results for experiments with very high rock/water ratios — say approximately 20/1 or higher — would be essentially the same as those obtained from experiments with comparatively low rock/water ratios.

### 3.5.5 Geochemical Effects of Alteration Corrosion of Waste Package Materials, Backfill, and Host Rocks

#### 3.5.5.1 Review

Geochemical conditions in the vicinity waste-package materials, backfill, and repository host rock will be determined principally by the extent to which these barrier materials react with heated groundwaters during the postclosure period. The major processes that act to change the compositions of ingressing groundwaters and alter solid materials in the disturbed zone of a groundwater-saturated repository are (1) dissolution of "unstable" solid phases by groundwater, and (2) precipitation and growth of new (secondary) solid phases that are more stable than the old (primary) solid phases under the geochemical conditions that have developed in the near field of the repository.

It is important to recognize that the presence of groundwater, rather than elevated repository temperature, is the principal catalyst for alteration of solid materials in the repository environment. This contention is supported by the results of experiments on packing material that have been

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performed at elevated temperatures in the absence of groundwater (PALMER 1983). Of particular concern in these experiments was the possibility that, upon heating to "high temperatures," bentonite in the packing material will suffer irreversible dehydration (loss of structural water) that would result in volume reduction and loss of swelling capacity. However, thermal dehydration curves for heat-treated bentonite prepared by Palmer et al. (1983) indicate that bentonite retains its structural water at temperatures up to 370°C for at least 340 d. This temperature is well above the maximum temperature that is expected to develop at the surfaces of canisters emplaced in an NWRB at the Hanford Site, so Palmer et al. (1983) concluded that dehydration of bentonite is unlikely to occur during the period of time after waste emplacement but before repository resaturation.

The influx of groundwater into the waste facility during the postclosure period is likely to have immediate effects on the packing material around waste canisters, because these materials are expected to be at elevated temperatures (due to the heat liberated from waste canisters) by the time that groundwater begins to resaturate the repository. The first likely effect is the swelling of the bentonite in the packing material, resulting in a significant decrease in the porosity and permeability of the material. These decreases should inhibit groundwater contact with waste canisters for a considerable period of time. However, it is to be expected that eventually, the basalt in the packing material will begin to alter to secondary minerals - principally clay minerals (smectite ± illite and zeolites - and basalt glass will begin to dissolve away. Subsequently, in one fashion or another, groundwater will come into contact with waste canisters, resulting in accelerated corrosion of the containers. Canister corrosion is likely to be manifested by the formation of layers of "films" of iron oxides along exposed metal surfaces, these layers gradually growing in thickness as corrosion proceeds. Furthermore, it is to be expected that canister corrosion will liberate some iron to the groundwater, and it is possible that this dissolution will: (1) induce the formation of iron-rich colloids (SHADE 1984), (2) promote further crystallization of iron-rich secondary minerals in the packing material, and (3) further diminish oxygen fugacity in the waste-package environment.

As temperatures rise in the near field during the early stages of the postclosure period, crushed basalt in backfill and the basaltic host rocks should begin to partially alter to secondary minerals, probably principally clay minerals and zeolites. (However, due to the lower temperatures of these materials compared to packing material, clay minerals that form by the alteration of basalt are apt to be mostly smectites rather than illites.) It is expected that the secondary minerals that crystallize in backfill and host rock will be very similar to the secondary minerals that occur naturally in the Grande Ronde basalt horizons (MYERS 1983).

Crystallization (and recrystallization) of secondary minerals will continue throughout the time that repository temperatures are rising, and probably also for some time after peak temperatures have been achieved. It is at this time, that is, probably hundreds of years after peak repository temperatures have been achieved, that initial breaching of waste canisters will occur. This event marks the conclusion of the containment period and

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the beginning of the isolation period. During the isolation period, additional breaching of canisters is expected, but concomitant increases in the total amount of HLW that is exposed to groundwater should be gradual. Therefore, it is unlikely that failure of waste canisters will have immediate or pronounced effects on geochemical conditions in an NWRB. If HLW is predominantly spent fuel (SF), then canister failure may tend to lower the redox state of exposed groundwaters, but SF is only sparingly soluble in groundwater, so it will probably have little effect on the solute content of exposed groundwaters (MYERS 1983). If, instead, HLW is predominantly borosilicate glass (vitrified commercial or defense HLW), more extensive waste/groundwater interaction is likely, but again the effects of breaching on geochemical conditions are not likely to be pronounced. The principal anticipated geochemical effects of interactions between borosilicate glass and groundwater are (1) partial dissolution of the borosilicate glass, and, simultaneously (2) an increase in the amounts of silica dissolved in exposed groundwaters. Finally, regardless of whether HLW is principally spent fuel or borosilicate glass, it is possible that solid materials and groundwaters in and around waste packages will be altered significantly by alpha radiation emanating from exposed waste. Of particular concern is the possibility that radiolytic reactions in groundwater will produce local oxidizing conditions and oxidized radionuclide species, thus counteracting — and perhaps negating — the purported mitigating effects (ostensibly "reducing" conditions) imposed by the basalt host rock.

#### 3.5.5.2 Assessment

BWIP experiments studies (e.g., APTED 1982b and PALMER 1983) have provided sufficient data to infer the overall pattern of postclosure alteration/corrosion of waste-package materials, backfill, and repository host rock in an NWRB at the Hanford Site. The principal questions concerning this topic that remain to be answered are fairly specific in nature. These are:

1. Besides temperature and the presence of groundwater, what are the parameters and processes that are most likely to impact the long-term porosity, permeability, and stability of packing material?
2. What are the geochemical consequences of sequential penetration of barrier materials by groundwater?
3. Will canister metal-groundwater reactions significantly reduce the redox conditions of groundwaters in and around basalt-hosted waste packages during the postclosure period?
4. What iron-rich solid phases are most likely to form as a result of canister corrosion?
5. To what extent are barrier materials in active "chemical communication" during the postclosure period?

In attempting to answer these questions, it will be important to properly account for the effects of kinetics on the dissolution/alteration of primary solid phases and the subsequent formation of secondary phases. The effects of kinetics on hydrothermal reactions must be known in order to accurately predict the kinds and quantities of solid phases that will be present in waste packages during the postclosure period.

### 3.5.6 Geochemical Effects of Radiation

#### 3.5.6.1 Review

Postclosure geochemical conditions in and around waste packages in an NWRB at the Hanford Site are expected to be influenced by gamma radiation emanating from waste canisters (DOE 1982, GRAY 1984). The principal expected effects are (1) radiolysis reactions in groundwater, and (2) radiolytic alteration ("damage") of exposed solid materials. Radiolysis reactions in groundwater that flows near waste packages are expected to be predominantly those that result from excitation and ionization (decomposition) of  $H_2O$ , the principal reaction products being: (1) short-lived radicals, that is, free electrons,  $H^+$ ,  $OH^-$ , and  $HO_2^-$ ; and (2) long-lived molecular products, that is,  $H_2$  and  $H_2O_2$  (DOE 1982). If  $H_2$  is able to escape from the irradiated groundwater after its formation, then the oxidation potential of the groundwater will be increased; otherwise (in a "closed system scenario"),  $H_2$  fugacity will remain high, this condition acting to (1) suppress further radiolysis reactions in the groundwater and (2) maintain redox conditions at levels near those of unexposed groundwater. Still other types of radiolysis reactions are possible when groundwaters contain significant amounts of dissolved solids or gases. For example, it has been demonstrated recently by Gray (1984) that radiolysis reactions in methane-bearing groundwaters produce polyethylene-like hydrocarbons. The nature and significance of this particular type of radiolysis reaction in Grande Ronde groundwater is currently being investigated further by BWIP.

The effects of radiation on solid materials — for example, loss of crystallinity and greater reactivity with heated groundwaters — appear to result principally from the creation of lattice imperfections (DOE 1982). Radiation effects on bentonite, basalt minerals, and basalt glass are not yet well understood, but they are not expected to be so extensive that they cause major changes in the mechanical and chemical characteristics of these solids.

#### 3.5.6.2 Assessment

The various types of fluid- and solid-state reactions that are likely to occur in the vicinity of waste canisters in an NWRB appear to be well established, but it is difficult to determine the significance of these reactions for assessments of the long-term stability and isolation performance of waste-package components and nearby host rocks. For example, it

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is highly uncertain whether aqueous species generated by radiolysis reactions will be present in large enough quantities (i.e., whether these species will be sufficiently long-lived) to significantly alter geochemical conditions in and around the waste packages in an NWRB. Likewise, while it is reasonable to expect that the solids in packing material immediately adjacent to waste canisters will be damaged by radiation, it is not clear how extensive this damage will be, or whether it will have any major impact on the stabilities of the solid materials and/or local geochemical conditions. The recent discovery of Gray (1984) that alpha-radiolysis reactions in methane-bearing groundwaters produce polyethylene-like hydrocarbons is intriguing and merits further investigation because it is possible that these hydrocarbons will have an important influence on (1) the rates at which radionuclides are released from waste packages, and (2) the mechanisms by which radionuclides are transported from waste packages toward the far field. Furthermore, it would seem to be worthwhile to determine the effects of alpha-radiolysis on local geochemical conditions, because this type of radiolysis should be more potent than gamma-radiolysis during the postcontainment period. It is clear that much work remains to be done to precisely determine the nature and significance of aqueous radiolysis reactions and radiolytic alteration of solids in and around waste packages in an NWRB at the Hanford Site.

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## 4. CONCLUSIONS, INFORMATION NEEDS, AND RECOMMENDATIONS

An evaluation of the available information on geochemical conditions at the Hanford Site indicates that there are six principal areas of technical investigations related to repository licensing which should receive further attention to ensure that acquisition of additional requisite data will proceed in an efficient and timely manner.

### 1. Additional information is needed on geochemical conditions along potential radionuclide release pathways at the Hanford Site.

At the present time there are insufficient field data available to unambiguously identify potential radionuclide-release pathways at the Hanford Site. This lack of data is a matter of concern for assessing the performance of this site, because satisfactory predictions of radionuclide release from a repository are contingent upon adequate knowledge of the effectiveness of radionuclide retardation mechanisms (e.g., solubility and sorption) along release pathways, and it may be difficult to demonstrate possession of this knowledge if there are any major uncertainties regarding the locations of radionuclide-release pathways and the geochemical conditions that prevail along these routes.

Geochemical information relating to radionuclide-release pathways that is required for defensible site-performance assessments includes: (1) the types, amounts, and characteristics of solid phases (basalt glass, primary minerals, and secondary minerals) that occur along the pathways; (2) redox conditions along the pathways; and (3) the quantities and compositions of "fresh" (uncontaminated) groundwaters that occur along the pathways. An accurate knowledge of the kinds and amounts of secondary minerals that occur along radionuclide-release pathways is essential for estimating the quantities of radionuclides that will be sorbed as radionuclide-bearing groundwaters travel through the site host rocks. Redox conditions along radionuclide-release pathways are important because they can influence the solubilities and sorptive properties of multivalent-state radionuclides. The presence of significant volumes of uncontaminated groundwater along radionuclide-release pathways is potentially important because it increases the likelihood of dilution of radionuclide-bearing groundwaters via (1) physical mixing of groundwaters, (2) matrix diffusion of radionuclides into the stagnant or slow-moving groundwater that occupies the pore spaces of rocks adjacent to the principal groundwater flow paths. Dilution of radionuclide-bearing groundwater would decrease the likelihood of supersaturation with radionuclides, which in turn might delay (or possibly prevent) the precipitation of radionuclide-bearing solids; however, this effect is probably more than counterbalanced by the increased sorption of radionuclides that is likely to occur as a result of matrix diffusion into uncontaminated groundwaters. Therefore, the overall effect of mixing of contaminated and uncontaminated groundwaters is likely to be a decrease in the rates of radionuclide transport toward the accessible environment.

2. A Conceptual model of postclosure groundwater resaturation of an NWRB at the Hanford Site is needed for predicting geochemical conditions in the NWRB during the postclosure period.

From discussions presented in recent reports (e.g., DOE 1982 and LONG 1983), it is evident that BWIP has yet to develop a realistic conceptual model of postclosure groundwater resaturation of an NWRB at the Hanford Site. Such a model is needed because assessments of repository system performance require detailed information on waste-canister corrosion, waste-form degradation, and radionuclide transport, and these phenomena occur at negligibly slow rates in the absence of groundwater. Furthermore, through its interactions with engineered barrier materials and the host rock, groundwater has profound effects on various geochemical parameters (e.g., redox conditions) that can strongly influence radionuclide migration. Therefore, a defensible conceptual model of groundwater resaturation of a repository is necessary for satisfactory predictions of near-field geochemical conditions in an NWRB during the postclosure period.

3. Additional information is needed on the role of basalt as a reductant in natural and synthetic basalt/groundwater systems at 50 to 300°C

Numerous BWIP reports [e.g., Apted and Myers (1982b), Wood et al. (1983)] have discussed the effects of redox conditions on (1) the containment performance of waste packages and (2) radionuclide transport and retardation mechanisms. In these reports it is stated that basalt will act as a reductant in the various geochemical environments of an NWRB at the Hanford Site, this behavior being manifested by (among other effects) slower rates of waste-canister corrosion, lower solubilities of multivalent-state radionuclides, and increased sorption of multivalent-state radionuclides. However, in order to fully document the ways in which redox conditions will influence the total isolation performance of an NWRB at the Hanford Site, it is necessary to have definitive answers to the following two key questions:

1. What is the nature of redox conditions in natural and synthetic basalt + groundwater ± secondary minerals systems at 50 to 300°C?
2. How do redox conditions affect the solubilities and sorptive properties of radionuclides?

Unfortunately, commentary and evidence presented in BWIP documents makes it clear that it is impossible to answer these questions completely at the present time.

The first major deficiency of BWIP information on redox conditions in basalt + groundwater ± secondary minerals systems is a lack of definitive data on ambient subsurface redox conditions at the Hanford Site. Eh values for Hanford Site groundwaters measured with platinum electrodes range from +0.35 to -0.2 V, a variability which may be due either to "poisoning" of



the platinum electrodes or to real variability in the Eh values. Evidently, DOE has chosen the former explanation, because on the basis of thermodynamic calculations (DOE 1982), Long (1983, Table I-50) suggests that "true" Eh of the groundwaters in candidate-repository horizons is  $-0.45 \pm 0.07$  V.

Another complicating factor in evaluating ambient redox conditions along potential radionuclide-release pathways at the Hanford Site is the possibility that local redox conditions may not be well poised ("buffered") by rock/groundwater interactions. Because reactions among aqueous species are frequently very sluggish at low temperatures, it is likely that redox reactions will not occur rapidly enough to maintain a "master" Eh that is immune to local physicochemical perturbations such as variations in the amounts and compositions of (1) glass and/or (2) secondary minerals in the host rocks. It would seem to be worthwhile to attempt to identify one or more redox couples that are "chemically active" (i.e., couples that are capable of reducing oxidized radionuclide species) in basalt + groundwater  $\pm$  secondary minerals systems at 50 to 60°C. This information would be useful in establishing how well poised redox conditions are in the basalt/groundwater systems at the Hanford Site.

Uncertainties similar to those associated with ambient redox conditions also arise in considering the nature and significance of Eh in basalt + groundwater  $\pm$  secondary minerals systems at "high temperatures" (90 to 300°C). Because of comparatively rapid rates of rock/groundwater reactions at high temperatures, a "system Eh" is apt to exist at 300°C, but this condition is unlikely to prevail at temperatures below 200°C. In any event, evidence presented by Wood et al. (1983) indicates that redox conditions are reducing in basalt/groundwater systems at high temperatures.

Because of the numerous difficulties associated with measuring/estimating Eh, it may be impractical to attempt to quantify a "system Eh" for basalt/groundwater systems. Instead, it would seem to be more advisable to attempt to determine experimentally how the presence of basalt  $\pm$  secondary minerals affects canister corrosion and the solubilities and sorptive properties of radionuclides. In particular, experiments are needed to establish whether basalt tends to lower the solubilities of multivalent-state radionuclides and increase the degree of sorption of these elements at 60 to 90°C. However, caution must be exercised in interpreting the results of experiments performed with crushed basalt, because comminution of the basalt will expose fresh surfaces of the rock and (therefore) speed up reactions greatly, so the conditions of experimentation may not be truly representative of basalt/groundwater environments in an NWRB.

4. Additional information is needed on the quantities of colloids and particulates that will be present in Hanford Site groundwaters during the postcontainment period.

The possibility that significant amounts of colloids and particulates may be formed during the postclosure period of an NWRB at the Hanford Site is

an important concern in developing conceptual models of radionuclide transport at the site, because it has been demonstrated that (1) colloids and particulates can remain suspended in groundwater for indefinite periods of time, and (2) many radionuclides are strongly sorbed by colloids and particulates (APPS 1982). Therefore, colloids and particulates may be principal vehicles by which radionuclides are transported from the engineered facility into the far field. It is likely, of course, that some fraction of these materials will eventually settle out or be filtered out during migration of groundwater through the rocks in the far field, but if groundwater flow is predominantly through fractures, flow tops, and interbeds at the Hanford Site, as is expected, then it is possible that this flow will be rapid enough and sufficiently unobstructed that significant amounts of radionuclide-bearing suspended matter will eventually be transported to the accessible environment. Because colloids and particulates can potentially play a significant role in radionuclide transport, the current lack of data on the formation and transport properties of these materials is a serious deficiency of the available body of technical information on anticipated geochemical conditions in the disturbed zone of an NWRB at the Hanford Site.

5. Additional information is needed on the degrees and rates of "chemical communication" among barrier materials in the disturbed zone of an NWRB at the Hanford Site.

BWIP conceptual models of waste-package performance and radionuclide transport are partly predicated on the assumption that groundwater flow through failed waste packages will occur by "sequential penetration" of engineered barriers. The general validity of this assumption is beyond doubt, but one fundamentally important question remains unaddressed: Over what distances are waste-package components, host rock, and groundwater in effective "chemical communication" as hydrothermal alteration proceeds during and after the containment period? This question is important because the kinds and amounts of solutes that can be dissolved in groundwater — including radionuclides — are determined in large measure by the geochemical conditions that prevail along groundwater flow paths. If certain geochemical conditions (e.g., redox conditions and pH) vary significantly along groundwater flow paths, then it can be expected that concentrations of many radionuclides in the groundwater will vary accordingly. On the other hand, if there is effective and rapid "chemical communication" among the various subregions of the engineered facility and surrounding disturbed host rock, then geochemical conditions are likely to be rather uniform along groundwater flow paths, and, consequently, groundwater compositions (and concentrations of dissolved radionuclides) are apt to vary smoothly both spatially and temporally. It is evident that knowledge of the degrees and rates of "chemical communication" among the various subregions of the engineered facility and the surrounding disturbed host rock is vital for establishing the consequences of sequential groundwater penetration of engineered barrier materials.

6. Additional information is needed concerning the effects of radiation on waste-package materials and groundwater in an NWRB at the Hanford Site.

A substantial body of direct and indirect evidence indicates that alpha and gamma radiation can have important effects on the solid materials and groundwater in and around waste packages housed in an NWRB at the Hanford Site. The most likely effects appear to be (1) physical and chemical degradation of solids, and (2) changes in the pH and redox conditions of groundwater. Solid materials damaged by prolonged exposure to radiation would not be in their lowest free-energy states, and, therefore, they would be more prone to chemical attack by heated groundwaters. Radiolysis of  $H_2O$  in groundwater could generate significant amounts of  $H_2O_2$  (DOE 1982), which would tend to elevate the oxidation state of the groundwater, thus (perhaps) enhancing the solubilities of multivalent-state radionuclides.

Additional effects of radiation appear to be possible when exposed groundwaters contain significant amounts of dissolved methane (GRAY 1984). It has been known for some time that many Hanford Site groundwaters contain small but significant quantities of dissolved methane, but it has been discovered recently that groundwaters beneath the current BWIP RRL contain very large amounts of dissolved methane (WINTCZAK 1984). BWIP has not had time to fully explore the ramifications of this discovery, but already some evidence indicates that it has important implications for conceptual models of radionuclide migration through the basaltic rocks at the Hanford Site. This possibility is suggested by experimental data obtained recently by Gray (1984), who discovered that radiolysis reactions in methane-bearing groundwater can lead to the formation of polyethylene-like hydrocarbons. Extrapolation of this result to the geochemical environments in the engineered facility of an NWRB implies that similar radiolysis reactions in  $CH_4$ -bearing groundwaters that flow past the waste packages in such a facility will, over time, produce significant quantities of polyethylene-like hydrocarbons. The presence of these hydrocarbons may be either advantageous or deleterious for waste-package performance depending on (among other factors) the quantities of hydrocarbons that are produced by radiolysis, the efficiency with which the hydrocarbons sorb radionuclides, and the distances that resulting radionuclide-bearing hydrocarbon material can be transported by groundwater.

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