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

Distribution:

DBrooks

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Dear Dave:

Enclosed is the final draft of the topical review "Review and Assessment of Radionuclide Solubility Information for the Basalt Waste Isolation Project Site." This report has been internally peer reviewed and edited. Please have the document technically reviewed as soon as possible so it can be published as an NRC NUREG report.

The comments in this report concerning the accuracy, completeness, and relevance of the available radionuclide solubility information for the Hanford Site are based on evaluations of pertinent BWIP documents published prior to October 1984. The report replaces earlier rough drafts submitted to NRC on June 12, 1984, and March 1984.

Sincerely,

Susan K. Whatley, Manager
Engineering Analysis and Planning
Chemical Technology Division

SKW:kk

Enclosure

cc: J. G. Blencoe
L. M. Ferris
G. K. Jacobs
A. D. Kelmers
D. C. Kocher
SKW File

w/o enc: A. P. Malinauskas
R. G. Wymer

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see folder for Mr. To
Brooks from Whalley
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REVIEW AND ASSESSMENT OF RADIONUCLIDE SOLUBILITY INFORMATION
FOR THE HANFORD, WASHINGTON, CANDIDATE HLW REPOSITORY SITE

J. G. Blencoe

Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Prepared for the
U.S. Nuclear Regulatory Commission
Office of Nuclear Materials Safety and Safeguards
Washington, DC 20555
under Interagency Agreement DOE 40-549-75

NRC FIN No. B0287

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

Draft

ABSTRACT

This report presents a review and assessment of information on radionuclide solubility that has been developed for, or pertains to, the Hanford, Washington, candidate high-level radioactive waste (HLW) repository site. Most of the technical investigations associated with determining the feasibility of constructing and operating a repository at this site are being performed or managed by the Basalt Waste Isolation Project (BWIP). Consequently, comments in this report concerning the accuracy, completeness, and relevance of available radionuclide solubility information for the Hanford Site are based principally on evaluations of pertinent BWIP documents published prior to the time of this writing (October 26, 1984).

BWIP information on the solubilities/concentrations of radionuclides in barrier materials + groundwater systems can be divided into two major categories: (1) experimental data on the solubilities/concentrations of radionuclides and radionuclide-analog elements in various waste form + groundwater ± basalt systems at 10 to 30 MPa, 90 to 300°C; and (2) calculated solubilities for radionuclides in basalt/groundwater systems at 1 atm, 25 to 90°C. Accordingly, the reviews and assessments of BWIP solubility data presented in this report have been divided into two parts — comments relating to experimental data for "high" temperatures (90 to 300°C), and comments concerning calculational data for "low" temperatures (25 to 90°C) — and within this expository framework the solubility data are described in terms of the system and temperature to which they pertain. The analyses of BWIP solubility data, in turn, provide the foundation for discussions of (1) the overall adequacy of BWIP solubility information, and (2) principal BWIP solubility-information needs.

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Review and Assessment of Radionuclide Solubility Information
for the Hanford, Washington, Candidate HLW Repository Site

J. G. Blencoe

1. EXECUTIVE SUMMARY

1.1 BWIP EXPERIMENTAL DATA ON THE SOLUBILITIES/CONCENTRATIONS OF
RADIONUCLIDES AND RADIONUCLIDE-ANALOG ELEMENTS IN BARRIER MATERIALS,
+ GROUNDWATER SYSTEMS AT 10 TO 30 MPa, 90 TO 300°C

Basalt Waste Isolation Project (BWIP) experimental data on the solubilities/concentrations of radionuclides and radionuclide-analog elements in barrier materials + groundwater systems at 10 to 30 MPa, 90 to 300°C, have been described by Apted and Myers (1982), Myers et al. (1983), and Coles (1983). The systems investigated to date are: simulated spent fuel + groundwater ± basalt, simulated commercial high-level waste (CHLW) borosilicate glass + groundwater ± basalt, ⁹⁹Tc-doped simulated CHLW borosilicate glass + groundwater ± basalt, ²³⁷Np- and ²³⁹Pu-doped simulated CHLW borosilicate glass + groundwater ± basalt, and simulated defense high-level waste (DHLW) borosilicate glass + groundwater + basalt. Experiments on these systems have yielded a small amount of data on the solubilities of the radionuclides ⁹⁹Tc, ²³⁷Np, and ²³⁹Pu, and a modest amount of data on the solubilities of the non-radioactive radionuclide-analog elements Mo, Ba, Sr, Cs, I, and U. Collectively, the data indicate that steady-state concentrations of radionuclides and/or radionuclide analog elements were achieved in many, but not all, of the experiments. The data also suggest that, in some of the experiments with radionuclide-analog elements, one or more of these elements reached a steady-state concentration prior to the cessation of experimentation, while in the same experiment the concentration of one

or more other radionuclide analog elements failed to achieve steady-state concentrations. Some other significant results of the experiments are as follows:

1. Data on the solubility of ^{99}Tc in the systems ^{99}Tc -doped simulated CHLW borosilicate glass + groundwater \pm basalt at 200°C indicate that, in the absence of basalt, ^{99}Tc reaches an apparent steady-state concentration of ~ 50 mg/L, but when basalt is present, the concentration of this radionuclide decreases to < 0.01 mg/L.
2. Data obtained from experiments with ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass + groundwater \pm basalt indicate that the apparent solubilities of ^{237}Np and ^{239}Pu are higher in basalt-present experiments. This result is attributable to the association of these radionuclides with filterable colloids and particulates which were formed in greater abundance in the basalt-present experiments.
3. Experimental data on the systems simulated spent fuel + groundwater + basalt and simulated CHLW borosilicate glass + groundwater + basalt indicate that, at a given temperature, the final relative concentrations of radionuclide-analog elements are typically $\text{Mo} > \text{Cs} > \text{I} > \text{Ba} > \text{Sr} > \text{U}$. Furthermore, for both simulated spent fuel and borosilicate glass systems, the experimental data suggest that the solubilities/concentrations of most radionuclide analog elements are lower when basalt is present.

1.2 CALCULATED SOLUBILITIES OF RADIONUCLIDES IN BASALT/GROUNDWATER SYSTEMS AT 1 ATM, 25 TO 60°C

Solubilities of radionuclides in basalt/groundwater systems at 1 atm, 25 to 60°C (EARLY 1982; EARLY 1984) have been obtained principally from

computer-code calculations using thermodynamic data for: (1) neutral and ionic aqueous species that are found (or have the potential to exist) in natural groundwaters, (2) major and minor rock-forming minerals, and (3) aqueous radionuclide species and radionuclide-bearing crystalline phases. Results of these calculations and theoretical considerations indicate that radionuclide solubilities are sensitive to: (1) groundwater composition, (2) Eh and pH, (3) the types and thermodynamic stabilities of radionuclide-bearing solid phases that are present, (4) temperature, (5) coprecipitation, and (6) the completeness and accuracy of the thermodynamic data base. For the range of groundwater compositions and Eh-pH conditions investigated by Early et al. (1984), the aqueous radionuclide species that are predicted to be dominant are hydroxy complexes (Zr, Pd, Sn, Sb, Sm, Eu, Th, U, Np, and Pu) and carbonate complexes (Ni, Sm, Eu, Pb, U, Np, Pu, and Am), while the solid phases which are predicted to control the solubilities of radionuclides are hydroxides and hydrous oxides (Pd, Sb, Sm, Eu, Pb, and Am), oxides (Ni, Sn, Th, Np, and Pu), pure elements (Se and Pd), and silicates (Zr and U). The calculations also indicate that the solubilities of Se, Pd, Sn, U, and Np exhibit the greatest sensitivity to Eh. For synthetic Grande Ronde groundwater GR-3 at 25°C and Eh = -0.3 V, calculations indicate that the relative solubilities (mol/L) of the radionuclides are Ni > Sb > Se > Pb > Am > Eu > Zr = Sm > Pu > U = Pd > Np > Th > Sn.

However, an assessment of the thermodynamic method for calculating the solubilities of radionuclides in basalt/groundwater systems at 1 atm, 25 to 90°C, indicates that this approach has the following drawbacks: (1)

the data bases for radionuclide solubility/speciation computer codes are incomplete and often contain thermodynamic data which are of dubious accuracy; (2) currently available radionuclide solubility/speciation computer codes cannot properly account for the chemical effects of radionuclide sorption, precipitation of radionuclide solid solutions, and/or sluggish reaction kinetics; (3) thermodynamic calculations of radionuclide solubilities performed to date are partly based on the assumption that redox equilibrium is achieved in basalt/groundwater systems, and this assumption is inconsistent with field and laboratory data on redox kinetics in rock/water systems at 1 atm, $T < 100^{\circ}\text{C}$; and (4) the types and compositions of radionuclide-bearing solids that will actually form in the disturbed zone and far field of a nuclear waste repository in basalt (NWRB) are not well known at the present time. In view of these difficulties it is evident that, by themselves, the results of thermodynamic calculations are insufficient to establish the true nature and significance of radionuclide solubility/speciation in basalt/groundwater systems.

1.3 ADEQUACY OF RADIONUCLIDE SOLUBILITY INFORMATION FOR ASSESSING THE PERFORMANCES OF ENGINEERED AND NATURAL BARRIERS IN AN NWRB AT THE HANFORD SITE

An evaluation of the information on radionuclide solubility that has been developed for the Hanford, Washington, candidate HLW repository site indicates that this information is insufficient to satisfy all of the technical criteria of NRC regulation 10 CFR 60. The principal apparent inadequacies of the information and pertinent items of concern are:

1. The relevancy of the solubility information to repository licensing requirements is uncertain because it remains to be determined what solubility information will be needed to conduct defensible performance assessment analyses and to satisfy the technical criteria and "reasonable assurance" requirement of 10 CFR 60.
2. Theoretical treatment of the solubility-vs.-time behavior of radionuclides in barrier materials + groundwater systems (APTED 1982a) is not supported by fundamental thermodynamic theory and pertinent experimental data.
3. Experimental data on the solubilities of radionuclides in barrier materials + groundwater systems at 90 to 300°C are sparse and were obtained under experimental conditions that do not adequately simulate the geochemical conditions which are expected to prevail in the vicinity of waste packages after the containment period.
4. Experimental data on the solubilities of radionuclides in basalt/groundwater systems at 25 to 90°C are very sparse.
5. Researchers concerned with acquiring and publishing experimental data on the solubilities/concentrations of radionuclides in barrier materials + groundwater systems have not yet developed appropriate methods for estimating the precision of their data.

1.4 INFORMATION NEEDS

An evaluation of the information on radionuclide solubility that is pertinent to the Hanford, Washington, candidate HLW repository site indicates that there are five principal areas of technical investigation which require further attention to ensure continued progress in acquiring radionuclide-solubility data that relates to repository licensing:

1. Additional simulated waste forms should be tested in "high-temperature" (90 to 300°C) hydrothermal experiments on waste form + groundwater ± basalt systems. Experiments with a variety of different simulated waste forms are needed to investigate the possibility that the solubilities/ concentrations of some radionuclides may be significantly altered by relatively small changes in the composition of the waste form.
2. Investigations of barrier materials + groundwater systems should include experiments in which hydrothermally altered basalt + bentonite mixtures (75% basalt + 25% bentonite) and pieces (not powders) of simulated canister and cladding material are among the solid starting materials. Experiments on systems that include these materials will simulate more accurately the geochemical environments in the vicinity of the waste packages in an NWRB after the containment period (nominally 300 to 1000 years after repository closure).
3. Investigations of barrier materials + groundwater systems should include hydrothermal experiments with fully radioactive waste forms because the results of these experiments will provide some of the data that are needed to determine whether radionuclide solubilities are strongly affected by radiolysis reactions.
4. Additional experimental data are needed for those radionuclides that have comparatively high solubilities in basalt/groundwater systems at 1 atm, 25 to 90°C.
5. Papers and reports that list and describe experimental data on radionuclide solubilities/concentrations should also present estimated limits of error for the data.

2. INTRODUCTION

2.1 REGULATORY CONTEXT OF SITE GEOCHEMICAL CONDITIONS INFORMATION

The Nuclear Waste Policy Act of 1982 defines the national program for disposal of civilian (commercial) high-level radioactive waste (HLW).^{*} In the Act, it is stipulated 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 that the repository will comply with applicable NRC and Environmental Protection Agency (EPA) regulations concerning radionuclide containment and release. For example, in NRC regulation 10CFR60.113 (NRC 1983) it is stipulated 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 40CFR191 (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

^{*}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.

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 fully document the contribution of individual processes and conditions which influence the performance of the repository system and its components.

Radionuclide solubility* is a technical issue in HLW repository-siting and performance-assessment activities because the quantities of radionuclides that are released from a repository are apt to be partly controlled by the solubilities of the radionuclides in the groundwaters at the repository site (NRC 1983). Significantly, this is likely to be the case for the proposed Hanford Site repository because current plans call for the waste facility to be constructed at a depth that is well below the local water table, and, therefore, it is to be expected that this facility will be flooded by groundwater within a few decades after repository closure. Thus, it is not surprising that BWIP technical activities presently include a vigorous data development program on the solubilities of radionuclides under both disturbed-zone ("high" temperature) and repository-ambient ("low" temperature) geochemical conditions.

*In this report, "solubility" will be understood to mean "steady-state, precipitation-limited, dissolved-plus-suspended aqueous concentration." The use of the word "concentration" will be restricted to those instances in which the amount of a dissolved-plus-suspended radionuclide is not controlled by the precipitation of one or more discrete solid phases; for example, when the aqueous concentration of a radionuclide is limited by sorption, or when the amount of dissolved-plus-suspended radionuclide is equal to the entire amount of that radionuclide that is present in a barrier materials + groundwater system. (In the latter case, the concentration of the radionuclide is said to be "inventory limited.")

2.2 GEOCHEMICAL CONTEXT OF RADIONUCLIDE SOLUBILITY INFORMATION

To properly predict the isolation performance of an HLW repository, it is necessary to identify and characterize all of the principal geochemical factors that will influence radionuclide-release rates. It is widely acknowledged that these factors include: (1) the nature and extent of chemical alteration and physical degradation of the engineered-system components and surrounding disturbed host rock; (2) the degree of waste-form alteration and dissolution; (3) the vehicles of radionuclide transport by groundwater (aqueous species, colloids, particulate matter) and the solubilities/concentrations of radionuclides in groundwater; (4) the efficiency with which engineered-system materials and host-rock minerals sorb radionuclides; and (5) the extent to which radionuclide-bearing groundwaters mix with uncontaminated groundwaters in the disturbed zone and far field. Therefore, the principal geochemical processes that would tend to deter release of radionuclides to the accessible environment are: (1) precipitation (low radionuclide solubility), (2) sorption (ion exchange, adsorption, chemisorption, etc.), (3) dilution and/or matrix diffusion, and (4) radioactive decay. However, it should also be borne in mind that the technical criteria of regulation 10CFR60.113 and the draft EPA standards for cumulative radionuclide release discussed in the preceding section of this report do not require complete characterization of all of these radionuclide-retardation processes, and the final set of processes selected by DOE to demonstrate compliance with applicable regulations may ultimately depend on the results of site-specific scenario and performance assessment analyses. Nevertheless, because many radionuclides have low solubilities

in groundwater, it is to be expected that waste package and site-performance assessments will frequently identify radionuclide solubility as a principal barrier to radionuclide release.

2.3 PURPOSE AND SCOPE OF THIS REPORT

This document provides the NRC with a review and assessment of published BWIP information on the solubilities/concentrations of radionuclides and radionuclide-analog elements in various barrier materials (waste form, basalt, etc.) + groundwater systems. Investigations of the solubilities of radionuclides by BWIP staff members and contractors are one aspect of the multifaceted BWIP mission to: (1) assess the feasibility of siting an HLW repository in the basalts that underlie the Hanford Site, and, should such feasibility be demonstrated, (2) develop and design the facilities and technologies that are required for the permanent isolation of HLW in basalt formations. The BWIP technical staff believes that the geochemical environments in an NWRB at the Hanford Site will be oxygen-deficient (reducing), and under such conditions the solubilities of many radionuclides (in particular, actinide elements) are very low; thus, it is likely that BWIP will attempt to take credit for this favorable geochemical condition in their attempts to demonstrate compliance with NRC and EPA regulations concerning containment and release of radionuclides from a mined HLW repository. Should this happen, it will be important for the NRC to be in a position to assess the accuracy, completeness, and relevance of BWIP information on the solubilities of radionuclides in barrier materials + groundwater systems. The principal purpose of this document is, therefore, to provide informational assistance to the NRC in the event of such an assessment.

2.4 BRIEF DESCRIPTION OF THE HANFORD SITE

The Hanford Site is located in southeastern Washington state, 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. Due to their high fluidity and large volume, the Columbia River basalts flowed for long distances from their source fissures, and in so doing 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/PRICE 1979; MYERS 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-km² 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 which 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 the present time, 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. PUBLISHED BWIP INFORMATION ON THE SOLUBILITIES OF RADIONUCLIDES AT 10 TO 30 MPa, 90 TO 300°C

3.1 BWIP APPROACH TO DATA DEVELOPMENT

A review of pertinent BWIP publications (APTED 1982a, 1982b; WOOD 1983, MYERS 1983; COLES 1983a; COLES 1983b) indicates that BWIP's program for hydrothermal testing of barrier materials — which includes measuring the solubilities of radionuclides in barrier materials + groundwater systems at 10 to 30 MPa, 90 to 300°C — is based on a number of important premises regarding: (1) expected postclosure events, geochemical conditions, and barrier materials/groundwater interactions in an NWRB at the Hanford Site, and (2) appropriate procedures for hydrothermal experiments on barrier materials + groundwater systems. These premises are described in the sections below.

3.1.1 BWIP-Cited Premises Concerning PostClosure Events, Geochemical Conditions, and Barrier Materials/Groundwater Interactions in an NWRB at the Hanford Site

The discussion items below, which are paraphrased from key BWIP reports (APTED 1982a, 1982b; MYERS 1983), describe various premises that have been adopted by BWIP staff members concerning postclosure events, geochemical conditions, and barrier materials/groundwater interactions in an NWRB at the Hanford Site.

1. An NWRB at the Hanford Site will be at atmospheric pressure during construction and waste package emplacement. After closure and groundwater resaturation, however, pressure will eventually return to ambient hydrostatic levels (~10 MPa).

2. Results of heat transfer calculations for various waste package configurations in an NWRB (ALTENHOFEN 1981; WESTINGHOUSE 1982) indicate that temperatures in the engineered facility will peak during the first 100 years after closure. If spent fuel is the principal waste form, postclosure repository temperatures in the very near field will increase from ambient levels (50 to 60°C) to a maximum of approximately 300°C (at the centers of waste packages), and thereafter will begin to fall slowly, requiring perhaps several hundred to several thousand years to fall below 100°C.

3. BWIP's approach to hydrothermal testing of barrier materials is based on the concept of sequential penetration of barriers by intruding groundwater. This concept holds that waste-form containment and the long-term stabilities and performances of barrier materials will be determined principally by chemical interactions with ingressing and egressing heated groundwaters. During the containment period, the waste canisters, packing material, and nearby host rock will be altered by hydrothermal activity. This alteration will be manifested by nucleation and growth of an assemblage of secondary solid phases that are more stable than the primary phases. Then, during the postcontainment or isolation period (i.e., after breaching of waste canisters), gradual alteration and dissolution of the waste form will begin, and, consequently, groundwater will become contaminated with radionuclides. These processes will be controlled or strongly influenced by the chemical reactivity of the waste form and nearby barrier materials. Most of the solid phases in the waste form, cladding, canister, and packing materials are not in their lowest free-energy states under the geochemical conditions that are expected to prevail during the isolation

period. Furthermore, at least some of these solid phases (especially those in the waste form) are liable to have suffered thermal and radiation damage, and, therefore, they will probably be more soluble than predicted by conventional thermodynamic calculations.

Consequently, it is likely that many of the solid phases in waste packages will readily react with groundwater to form new and more stable solid phases. Elevated temperatures and radiation levels during the early postcontainment period may also lead to enhanced groundwater solubilities of many radionuclides. However, it is to be expected that continued nucleation and growth of secondary minerals/solid phases within the waste package, backfill, and basalt will tend to decrease the solubilities of radionuclides to low levels. Also, while waste form/groundwater reactions will probably control geochemical conditions (e.g., redox state and pH of the groundwater) in the environment immediately around the waste form, it is to be expected that this control will shift back to basalt as the radionuclide-bearing groundwater flows away from the waste form.

4. Migration of contaminated groundwater is the most credible mechanism of radionuclide transport. Therefore, defensible predictions of long-term radionuclide release rates from the waste packages in an NWRB require knowledge of the solubilities of radionuclides under site-specific conditions. Reactions between radionuclide-bearing groundwater, secondary minerals/solid phases, and basalt, as well as the rate of flow of groundwater, will determine the rates of radionuclide release from waste packages. Subsequent transport of dissolved radionuclides will occur down thermal gradients in the backfill and repository host rock. As temperature decreases with increasing distance from the waste packages,

the solubilities of most radionuclides will decrease; therefore, provided that there is little or no mingling of contaminated groundwaters with fresh, uncontaminated groundwaters, the contaminated groundwaters will become supersaturated with radionuclide elements, and one or more radionuclide-bearing solid phases should begin to precipitate. As transport processes carry remaining dissolved radionuclides beyond the region of thermal perturbation around the waste facility, additional precipitation of radionuclide-bearing solid phases may occur in response to decreases in temperature and/or to local variations in groundwater chemistry. It is also to be expected that sorption of radionuclides by primary and/or secondary minerals in the basalt host rock will tend to reduce the concentrations of these elements in contaminated groundwaters.

3.1.2 BWIP-Cited Premises Concerning Procedures for Hydrothermal Experiments on Barrier Materials + Groundwater Systems

The discussion items below, which are paraphrased from key BWIP reports (APTED 1982a, 1982b; MYERS 1983), describe premises which, taken together, comprise the philosophical framework of BWIP's experimental program on barrier materials + groundwater systems at high temperatures.

1. Because it is anticipated that groundwater flow through the waste packages in an NWRB will be extremely slow, evaluations of waste form performance and calculations of the long-term release rate of radionuclides should be based on experimental measurements of radionuclide solubility limits which are established or influenced by radionuclide-bearing solids that persist or form during hydrothermal alteration of

the waste form. Therefore, BWIP's program for hydrothermal testing of waste forms emphasizes measuring the solubilities (steady-state concentrations) of radionuclides, not the leach rates of these elements. It is expected that tests conducted for durations sufficient to attain an initial steady-state groundwater composition will yield solubilities for radionuclides which are more conservative (higher) than the solubilities which are expected to control long-term release rates.

2. In its program of hydrothermal testing of waste forms, BWIP has adopted a "fate-of-radionuclides" approach, as opposed to an approach that only deals with the resistance of the waste form to structural and chemical changes. One of the principal goals of the "fate-of-radionuclides" approach is to determine which solid phases control the solubilities of radionuclides.

3. Waste form/groundwater interactions will be examined experimentally both with basalt present and with basalt absent under repository-specific conditions. Basalt-present experiments will more closely simulate the chemical conditions in an NWRB, because basalt is the volumetrically dominant reactive material in the repository, and crushed basalt will be the major component of the packing material. It is believed that basalt can buffer the composition, redox state, and pH of groundwaters. Basalt will also be an important source of Si, Fe, Mg, Al, and K, the presence of which will promote the crystallization of important secondary minerals (e.g., clay minerals and zeolites) which may exert considerable control on steady-state concentrations of radionuclides.

4. In their initial (unaltered) forms, both simulated spent fuel and borosilicate glass are in a more oxidized state than basalt. Therefore, it is to be expected that these waste forms will tend to elevate the redox state of coexisting groundwater relative to the redox state that would exist if basalt was the only solid material that was present. Nevertheless, the BWIP staff believes (MYERS 1983) that relatively reducing conditions prevail during hydrothermal experiments. The "buffering mechanism" is inferred to be the dissolution of Fe^{2+} -bearing glass in the basalt, oxidation of the resulting aqueous Fe^{2+} ions to Fe^{3+} ions, followed by precipitation of ferric oxides, hydroxides, or oxyhydroxides, and silica.

5. Performing experiments with simulated waste forms and obtaining measurements of the solubilities/concentrations of radionuclide-analog elements in simulated waste form + groundwater \pm basalt systems constitute a preliminary basis for evaluating the radionuclide-containment performances of fully radioactive waste forms. [In a simulated waste form, nonradioactive elements or isotopes ("radionuclide analogs") are substituted for the radioactive elements or isotopes which are present in a corresponding "real" waste form.] The use of simulated waste forms has an immediate practical advantage: a hot cell is not required either before, during, or after experimentation. Therefore, experiments with these materials are beneficial for evaluating the experimental equipment and techniques that will eventually be used to obtain data on the release of radionuclides from fully radioactive waste forms. Furthermore, data obtained from experiments on simulated waste forms will help to identify radionuclides that (1) have high solubilities,

(2) display complex chemical behavior under hydrothermal conditions, and/or (3) may require special analytical attention. Data from tests using simulated waste forms will eventually be superseded by data obtained from experiments performed on systems that include a fully radioactive waste form.

6. Because variations in pressure over the range 10 to 30 MPa do not significantly affect chemical reactions between condensed phases, the BWIP has selected a standard pressure of 30 MPa for most of its hydrothermal experiments. The only exception to this practice is the testing of DHLW borosilicate glass; for systems containing this simulated waste form, the BWIP and the Savannah River Laboratory have agreed to perform experiments at 10 MPa.

7. It is well established that: (1) increasing the temperature of laboratory tests can dramatically increase the rates of hydrothermal reactions, and (2) results obtained at high temperatures can, in many instances, be extrapolated to low temperatures where time constraints may prohibit satisfactory experimental testing. (However, the dissolution/growth mechanisms operative at high and low temperatures may not be the same.) Furthermore, data obtained from experiments performed at temperatures as high as 300°C are required to model radionuclide-release scenarios based on premature canister failure. Therefore, and in view of the results of heat transfer calculations for various waste package configurations in an NWRB (ALTENHOFEN 1981; WESTINGHOUSE 1982), the BWIP has selected 50 to 300°C as an appropriate temperature range for hydrothermal testing of barrier materials.

8. It is well known that rates of chemical reactions in rock/water experiments can be accelerated by fine grinding of solid starting materials. Comminution greatly increases the reactive surface area (or reactive surficial mass) of the solids, and this typically reduces the time required for the formation and growth of new and more stable solid phases. The large ratio of surface area to total mass of the solids which is created by grinding ensures that, to a first approximation, the entire mass of solid will be the effective reactive mass. The resulting acceleration of reaction rates should not affect the final steady-state phase assemblage, only the time that is required to reach final steady-state conditions.

9. The relative amounts of rock and groundwater in hydrothermal tests will not significantly affect experimental results, provided that the rock/groundwater ratio is greater than approximately 1:50.

3.2 REVIEW OF PUBLISHED BWIP SOLUBILITY INFORMATION

3.2.1 Experimental Results

This section presents: (1) summaries of BWIP information on the solubilities/concentrations of radionuclides and radionuclide-analog elements in waste form + groundwater ± basalt systems at 90 to 300°C, and (2) an itemized listing of additional important information that BWIP staff members and contractors have obtained from their hydrothermal experiments. The summaries and interpretations given here result from the writer's independent assessment of the solubility/concentration data listed by BWIP staff members and contractors (MYERS 1983; COLES

1983b). Corresponding interpretations of these data by BWIP staff members and contractors — which in many instances are at variance with statements and conclusions presented in this section — are summarized in Tables B.1-B.5 in Appendix B. (See Appendix B for a complete explanation.)

3.2.2 Key BWIP Information on the Solubilities of Radionuclides and Radionuclide-Analog Elements at 90 to 300°C

3.2.2.1 Technetium-99

Data on ^{99}Tc have been obtained from experiments on the systems ^{99}Tc -doped simulated CHLW borosilicate glass + groundwater ± basalt (P = 30 MPa, T = 200°C) (MYERS 1983; COLES 1983b).

1. The system ^{99}Tc -doped simulated CHLW borosilicate glass + groundwater. Technetium-99 achieved an apparent steady-state concentration of ~50 mg/L.
2. The system ^{99}Tc -doped simulated CHLW borosilicate glass + groundwater + basalt. Technetium-99 first reached an apparent steady-state concentration of ~2.5 mg/L, but thereafter decreased to a negligibly small concentration (<0.01 mg/L).

3.2.2.2 Neptunium-237

Data on ^{237}Np have been obtained from experiments on the systems ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass + groundwater ± basalt (P = 30 MPa, T = 200°C) (COLES 1983b).

1. The system ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass + groundwater. Neptunium-237 achieved an apparent steady-state concentration of ~0.0025 mg/L.

2. The system ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass + groundwater + basalt. Neptunium-237 achieved an apparent steady-state concentration of ~ 0.031 mg/L.

3.2.2.3 Plutonium-239

Data on ^{239}Pu have been obtained from experiments on the systems ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass + groundwater \pm basalt (P = 30 MPa, T = 200°C) (COLES 1983b).

1. The system ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass + groundwater. Plutonium-239 achieved an apparent steady-state concentration of ~ 0.0001 mg/L.

2. The system ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass + groundwater + basalt. The concentration of ^{239}Pu reached a maximum value of 0.0072 mg/L, but thereafter decreased to ~ 0.0034 mg/L.

3.2.2.4 Molybdenum

Nonradioactive molybdenum is an analog for the radioactive isotopes of technetium (e.g., ^{99}Tc). Data on molybdenum have been obtained from experiments on the systems simulated spent fuel + groundwater \pm basalt (P = 30 MPa, T = 100, 200, and 300°C) and simulated CHLW borosilicate glass + groundwater \pm basalt (P = 30 MPa, T = 100, 200, and 300°C) (MYERS 1983).

1. The systems simulated spent fuel + groundwater \pm basalt. Molybdenum is dissolved rapidly from simulated spent fuel and appears to be somewhat less soluble when basalt is present. In the absence of basalt, the concentrations of molybdenum appear to increase with increasing temperature (final concentrations were ~ 80 , ~ 68 , and ~ 136 mg/L at 100, 200,

and 300°C, respectively), whereas with basalt present, molybdenum concentrations systematically decrease with increasing temperature (final concentrations were ~75, ~49, and ~19 mg/L at 100, 200, and 300°C, respectively).

2. The systems simulated CHLW borosilicate glass + groundwater ± basalt. Molybdenum is rapidly dissolved from CHLW borosilicate glass, and, as was observed in the simulated spent fuel systems, the presence of basalt tends to decrease the concentrations of molybdenum. (However, molybdenum is much more soluble in CHLW systems than in simulated spent fuel systems.) Whether basalt is present or absent, the concentrations of molybdenum tend to increase with increasing temperature. (Final concentrations of molybdenum in basalt-present experiments were ~412, ~650, and ~1300 mg/L at 100, 200, and 300°C, respectively. Final concentrations of molybdenum in basalt-absent experiments were ~69, ~161, and ~600 mg/L at 100, 200, and 300°C respectively.) Amounts of dissolved molybdenum appear to be very sensitive to the type of CHLW glass that is used in experimentation.

3.2.2.5 Barium

Nonradioactive barium is an analog for the radioactive isotopes of radium (e.g., ^{226}Ra). Data on barium have been obtained from experiments on the systems simulated spent fuel + groundwater ± basalt (P = 30 MPa, T = 100, 200, and 300°C) and simulated CHLW borosilicate glass + groundwater ± basalt (P = 30 MPa, T = 100, 200, and 300°C) (MYERS 1983).

1. The systems simulated spent fuel + groundwater ± basalt. Data for the system simulated spent fuel + groundwater indicate that barium reached steady-state concentrations during the experiments, and these

concentrations decrease with increasing temperature (~0.30, ~0.12, and ~0.05 mg/L at 100, 200, and 300°C, respectively). Data obtained from basalt-present experiments are incomplete and exhibit no discernable trends.

2. The systems simulated CHLW borosilicate glass + groundwater ± basalt. Barium concentration vs time data for these systems are similar to corresponding data obtained from simulated spent fuel systems. Final concentrations in both basalt-present and basalt-absent experiments performed at 200 and 300°C fall in the narrow range 0.05 to 0.10 mg/L. Concentrations in experiments performed at 100°C are systematically higher, but these concentrations appear to have been decreasing at the time that experimentation was concluded [final measured concentrations were 1.08 mg/L (basalt-absent) and 0.47 mg/L (basalt-present)].

3.2.2.6 Strontium

Nonradioactive strontium is a substitute for the radioactive isotopes of strontium (e.g., ⁹⁰Sr). Data on strontium have been obtained from experiments on the systems simulated spent fuel + groundwater ± basalt (P = 30 MPa, T = 100, 200, and 300°C), simulated CHLW borosilicate glass + groundwater ± basalt (P = 30 MPa, T = 100, 200, and 300°C), and simulated DHLW borosilicate glass + basalt + groundwater (P = 10 MPa, T = 90 and 150°C) (MYERS 1983).

1. The systems simulated spent fuel + groundwater ± basalt. In the system simulated spent fuel + groundwater, the concentration of strontium decreased slightly (from ~0.16 to ~0.05 mg/L at 100°C) or remained essentially constant (~0.09 mg/L at 300°C) during experimentation. In experiments performed on the system simulated spent fuel + groundwater +

basalt, strontium concentrations increased at first, but thereafter gradually returned to their initial values (initial and final concentrations were ~0.2, ~0.3, and ~0.2 mg/L at 100, 200, and 300°C, respectively).*

2. The systems simulated CHLW borosilicate glass + groundwater ± basalt. In experiments performed on the system simulated CHLW borosilicate glass + groundwater at 200 and 300°C, strontium concentrations rose from initial values of 0 mg/L to apparent steady-state concentrations of ~0.10 and ~0.04 mg/L, respectively. Concentrations in the experiment performed at 100°C are systematically higher, but these concentrations appear to have been decreasing at the time that experimentation was concluded (the final concentration was ~0.73 mg/L). Similar results were obtained in experiments on the system simulated CHLW borosilicate glass + groundwater + basalt. At 200 and 300°C, strontium concentrations rose from initial values of 0 mg/L to apparent steady-state concentrations of ~0.02 and ~0.01 mg/L, respectively. Concentrations in the experiment performed at 100°C are systematically higher, but these concentrations appear to have been decreasing at the time that experimentation was concluded (the final concentration was ~0.28 mg/L). Taken together, the experimental data indicate that basalt tends to reduce the amounts of dissolved strontium in simulated CHLW borosilicate glass systems.

*Here and in subsequent commentary, the "initial concentration" of a nuclide in a hydrothermal experiment refers to the dissolved-plus-suspended concentration of that nuclide in synthetic groundwater at, or shortly after, the time that desired pressure-temperature conditions were achieved in the experiment.

3. The system simulated DHLW borosilicate glass + groundwater + basalt. Strontium concentrations, initially 0 mg/L, rose to apparent steady-state concentrations of ~0.005 mg/L and ~0.003 mg/L at 90 and 150°C, respectively. However, at 150°C, there is some evidence that the concentration of strontium was increasing at the very end of the experiment (the final measured concentration was 0.018 mg/L).

3.2.2.7 Cesium

Nonradioactive cesium is a substitute for the radioactive isotopes of cesium (e.g., ^{135}Cs and ^{137}Cs). Data on cesium have been obtained from experiments on the system simulated spent fuel + groundwater + basalt (P = 30 MPa, T = 100, 200, and 300°C) (MYERS 1983).

At 100°C, the concentration of cesium rose quickly to an apparent steady-state concentration of ~50 mg/L. At 200°C, the concentration of cesium rose to a maximum value of ~109 mg/L, and subsequently decreased to an apparent steady-state concentration of ~30 mg/L. At 300°C, the concentration of cesium at first rose sharply to ~48 mg/L, then decreased erratically to ~11 mg/L, and thereafter gradually increased again to ~47 mg/L.

3.2.2.8 Iodine

Nonradioactive iodine is a substitute for the radioactive isotopes of iodine (e.g., ^{129}I). Data on iodine have been obtained from experiments on the system simulated spent fuel + groundwater ± basalt (P = 30 MPa, T = 100, 200, and 300°C) (MYERS 1983).

At 100°C, the concentration of iodine increased rapidly to an apparent inventory-limited concentration of ~11 mg/L. At 200°C, data for iodine are of suspect validity and are being disregarded by BWIP staff members. At 300°C, the concentration of iodine at first rose sharply to an apparent steady-state concentration of ~4 mg/L, but later increased again to an apparent inventory-limited concentration of ~11 mg/L.

3.2.2.9 Uranium

Data on uranium have been obtained from experiments on the system simulated spent fuel + groundwater ± basalt (P = 30 MPa, T = 100, 200, and 300°C) (MYERS 1983).

At 100°C, the concentration of uranium at first rose sharply to a maximum concentration of ~1.2 mg/L, and thereafter decreased to an apparent steady-state concentration of ~0.3 mg/L. At 200°C, the concentration of uranium initially rose quickly to ~1.6 mg/L, and thereafter steadily decreased to ~0.1 mg/L. Data for uranium at 300°C are sparse, but apparently a steady-state concentration of ~0.1 mg/L was achieved during experimentation.

3.2.3 Additional Significant Experimental Information

In addition to providing data on the solubilities/concentrations of radionuclides and radionuclide-analog elements in waste form + groundwater ± basalt systems, the hydrothermal experiments performed by BWIP staff members and contractors have yielded a wealth of ancillary information on: (1) the concentration vs time behavior of the major solute elements (e.g., sodium and silicon) in barrier materials + groundwater

systems, and (2) the solid phases that form or persist during barrier materials + groundwater experiments. The discussion items below, which are paraphrased from key BWIP reports (APTED 1982b; MYERS 1983; COLES 1983b), describe some of the more important results that were obtained in these experiments.

1. Compositional and structural differences between spent fuel and borosilicate glass are reflected in the significantly different radionuclide-release performances of these two waste forms. In general, the major elements of simulated spent fuel are sparingly soluble in synthetic groundwater. Thus, the major-element chemistry of groundwater in contact with this waste form does not change greatly during experiments performed at 100 to 300°C. By contrast, and due to its greater intrinsic metastability, borosilicate glass displays a high degree of reactivity with groundwater. In particular, the solubilities of Si, Na, B, and Mo are much higher in borosilicate glass + groundwater ± basalt systems than in spent fuel + groundwater ± basalt systems. This observation is partly attributable to the fact that different primary and secondary solid phases control or influence the groundwater solubilities of radionuclides in these two very different types of systems.

2. Results obtained from hydrothermal experiments on both simulated spent fuel systems and borosilicate glass systems are significantly different when basalt is present. These differences are partly attributable to the fact that basalt contains Mg, Fe, Al, and K, which are not present (or are present in much smaller amounts) in the waste forms, and the presence of these components tends to favor the formation of secondary minerals/solid phases that either control or strongly

influence the composition of coexisting groundwater. At a given experimental temperature (e.g., 200°C, and especially 300°C), the principal effect of adding basalt to the system simulated spent fuel + groundwater is to increase the amount of dissolved silicon; the concentrations of other solute elements remain more or less unchanged. By contrast, for borosilicate glass systems, the principal effect of adding basalt is to decrease the concentrations of Si, Na, and B. Comparing the results obtained from experiments on spent fuel + groundwater ± basalt systems with corresponding results obtained from experiments on borosilicate glass + groundwater ± basalt systems, it is evident that, in particular, the solubilities of Si, Na, B, and Mo are much higher in borosilicate glass + groundwater ± basalt systems than in spent fuel + groundwater ± basalt systems. On the other hand, regardless of the type of waste form and the presence or absence of basalt, initial groundwater concentrations of fluorine and chlorine remain essentially unchanged. This result indicates that, in contrast to other major solute elements, fluorine and chlorine do not interact chemically with solid phases to any significant extent.

3. For all waste form + groundwater ± basalt systems, it is observed that, even when some solute elements apparently achieve steady-state concentrations, the concentrations of other elements continue to change, indicating that, throughout the course of experimentation, primary solid phases continue to dissolve, and secondary minerals/solid phases continue to crystallize. Consequently, saturation of groundwater with silicon (or any other nonradioactive element) does not preclude subsequent release (dissolution) of radionuclides from a waste form as has been hypothesized by some investigators.

4. In general, experiments at 300°C produce a greater variety of secondary minerals/solid phases than do corresponding experiments performed at 200°C. This result is attributable to a slower rate of nucleation and growth of secondary solid phases at lower temperatures.

5. Some of the secondary minerals (e.g., clay minerals and zeolites) that formed in basalt-present systems during hydrothermal experiments conducted at 300°C are also minerals that occur in the basalts that underlie the Hanford Site. This result suggests that these alteration minerals are "steady-state" crystalline phases which will form and persist in the repository environment for many thousands of years.

6. Data on the 25°C pHs of synthetic groundwaters obtained from waste form + groundwater ± basalt experiments do not provide an accurate indication of the pHs that prevailed during experimentation; specifically, at a given temperature and time of experimentation, pH at experimental conditions may be either higher or lower than the pH that is measured at 25°C.

7. According to calculations performed with the computer code HIPH4, at $T < 100^{\circ}\text{C}$ the pH of groundwater in the system basalt + groundwater is controlled by the silicic acid and bicarbonate buffers, while at $T > 100^{\circ}\text{C}$ the dissociation of water is the predominant pH buffering reaction. However, the results of 25°C pH measurements on synthetic groundwaters obtained from waste form + groundwater ± basalt experiments indicate that waste forms may significantly influence pH during experimentation. For example, Myers et al. (1983) suggest that, at 300°C, simulated spent fuel reacts with groundwater in a manner that causes pH to decrease.

Also, 25°C pH data described by Myers et al. indicate that, among other effects, the dissolution of borosilicate glass causes pH to rise to levels above those achieved in basalt + groundwater experiments.

8. Generally, reproducibility of the results obtained from hydrothermal experiments is good, but in some cases the data exhibit an apparent functional dependence on the initial physical states of the solid starting materials. For example, results obtained from experiments performed on the system simulated spent fuel + groundwater + basalt (MYERS 1983) suggest that changes in the concentration of CO_3^{2-} during experimentation were influenced by the initial grain size of the basalt. Also, when a single piece (monolith) of DHLW glass was used as the starting waste form material for a 100°C experiment on the system simulated DHLW borosilicate glass + groundwater + basalt (MYERS 1983), it was observed that resulting 25°C pH data for the groundwater contrasted markedly with corresponding data obtained from experiments conducted at 90 and 150°C using crushed DHLW glass.

3.2.4 Calculational Results

To date, there is no evidence of attempts by BWIP staff members and contractors to calculate the solubilities of radionuclides in barrier materials + groundwater systems at "high" temperatures (90 to 300°C). It is likely that these calculations have not been performed for reasons that are discussed in detail in Sects. 4.3 and 4.4 of this report.

3.3 BWIP-CITED LIMITATIONS OF THEIR SOLUBILITY INFORMATION

Apted and Myers (1982b) and Myers et al. (1983) cite the following important limitations of BWIP experimental data on the solubilities of radionuclides at 90 to 300°C.

1. The synthetic groundwaters used in hydrothermal experiments performed by BWIP staff members and contractors are compositional models for the natural (ambient) groundwaters that occur in Grande Ronde Basalt horizons. However, the groundwaters that will eventually come into contact with the radioactive waste in an NWRB at the Hanford Site are likely to have compositions which are significantly different from those of ambient groundwaters. These differences are likely because groundwater that comes into contact with waste in an NWRB must first pass through hydrothermally altered basalt and then penetrate a series of engineered barrier materials before it reaches the waste form. Groundwaters flowing along such paths will experience an increase in temperature as the waste form is approached, so it is to be expected that the chemistries of these groundwaters will be extensively modified by reactions with the solid materials that are transgressed.
2. Methods have not yet been devised to directly or indirectly determine groundwater Eh (redox potential) in barrier materials + groundwater experiments.
3. Calculated pHs for groundwaters in barrier materials + groundwater systems at temperatures above 100°C may be significantly inaccurate due to: (1) an incomplete knowledge of all of the different aqueous

reactions that can occur in such systems at high temperatures, and (2) difficulties in extrapolating values for thermodynamic parameters (e.g., equilibrium constants) from low temperatures (~25°C) to high temperatures.

4. Canister materials have not yet been included in BWIP hydrothermal experiments. It is likely that these materials will react chemically with the waste form, basalt, and/or groundwater in hydrothermal experiments, thereby producing effects which cannot be predicted from results of waste form + groundwater ± basalt experiments.

5. To date, BWIP staff members and contractors have not performed any hydrothermal experiments with fully radioactive waste forms.

3.4 ASSESSMENT OF BWIP SOLUBILITY INFORMATION

This section contains various comments by the writer concerning the nature and significance of BWIP information on the solubilities of radionuclides in barrier materials + groundwater systems at 90 to 300°C.

1. Concentration vs time behavior of solute elements — Collectively, the data obtained from barrier materials + groundwater experiments indicate that the solubilities/concentrations of individual solute elements (including radionuclides and radionuclide-analog elements) in closed isobaric, isothermal, barrier materials + groundwater systems may either increase or decrease with time. Furthermore, it is evident that one or more solute elements may reach apparent steady-state concentrations prior to the cessation of experimentation, while in the same experiment the concentrations of one or more other elements may fail to achieve

steady-state concentrations. The complicated concentration vs time behavior of some solute elements may in certain cases be due to analytical errors and/or the presence of important amounts of colloidal material in the synthetic groundwaters, but in many instances it is likely that the observed erratic behavior is truly representative of the concentration vs time characteristics of the nuclide for a given set of experimental conditions (system, bulk composition, pressure, temperature, etc.).

2. The significance of radionuclide sorption by mineral crystalline solutions — The effects of solid-phase dissolution and precipitation on the compositions of groundwaters and the solubilities of radionuclides are emphasized in BWIP publications, but the potentially significant effects of mineral/groundwater ion exchange are usually deemphasized. This bias is unfortunate, because it is firmly established that certain mineral crystalline solutions — in particular, clay minerals and zeolites — will readily sorb many different kinds of radionuclides. Furthermore, in certain circumstances, radionuclide sorption by mineral crystalline solutions can forestall or preclude the precipitation/crystallization of discrete radionuclide-rich solid phases.

3. The effects of basalt on the solubility of ^{99}Tc — Evidently, the presence of basalt has a profound effect on the solubility of ^{99}Tc in simulated CHLW borosilicate glass systems. In the presence of basalt, ^{99}Tc reached a steady-state concentration which is approximately three orders of magnitude lower than the concentration that is reached when basalt is absent. This result can be explained in two ways: (1) the basalt may be lowering redox conditions to a point that ^{99}Tc exists in a

low oxidation state, thereby reducing its solubility or promoting adsorption onto primary or secondary solid phases (e.g., iron-bearing solid phases); or (2) hydrothermal alteration of basalt leads to the formation of one or more secondary solid phases which incorporate ^{99}Tc into their crystal structures.

4. The effects of waste form composition on data obtained from barrier materials + groundwater experiments - It would be useful to investigate the possibility that the data obtained from barrier materials + groundwater experiments can be affected significantly by relatively small changes in the composition of the waste form. In particular, it would be important to determine whether or not the solubilities/concentrations of radionuclides can be altered significantly by such changes.

5. The use of freshly ground basalt in waste form + groundwater + basalt experiments - The use of freshly ground basalt as a solid starting material in waste form + groundwater + basalt experiments would seem to be ill-advised because the crushed basalt in the packing material of waste packages of an NWRB will almost certainly be partly to mostly altered to secondary minerals by the end of the containment period. Therefore, hydrothermally altered basalt, not freshly ground "unreacted" basalt, should be used in these experiments.

6. Precision of radionuclide solubility data - Determinations of the true characteristics and significance of hydrothermal data on the solubilities/concentrations of radionuclides and radionuclide-analog

elements in barrier materials + groundwater systems are made more difficult by the fact that there have been no attempts to determine statistically valid uncertainties (confidence levels) for the data. The precision of data should always be either determined statistically — if it is possible to do so — or (at least) estimated empirically.

7. Some comments concerning "the Volkswagen diagram" — There are three confusing aspects of figure 2 in Apted (1982a) (see Fig. 1). (For reasons which are readily apparent upon examining this figure, it is frequently referred to as "the Volkswagen diagram.") This figure is important because it illustrates graphically what BWIP staff members are claiming is a general rule-of-thumb concerning the concentration-vs-time behavior of dissolved radionuclides.

First, Apted does not indicate specifically that the figure refers to reactions/equilibria in a closed, isobaric, isothermal system. This must be the situation because, otherwise, much of the explanatory discussion that he presents is either misleading or erroneous.

Second, the figure indicates that, after a sufficient period of time — specifically, after time t_c — a series of steady states are reached, and for each steady state the concentrations of solutes remain more-or-less constant. As noted by Apted, these "solubility limits" of metastable phases actually represent transitory periods during which time a delicate balance exists between dissolution, precipitation, and ion exchange. However, because the rates of these reaction processes can be affected by such variables as the surface areas of solid phases, the kinetics of nucleation and growth of precipitated crystals, etc.,

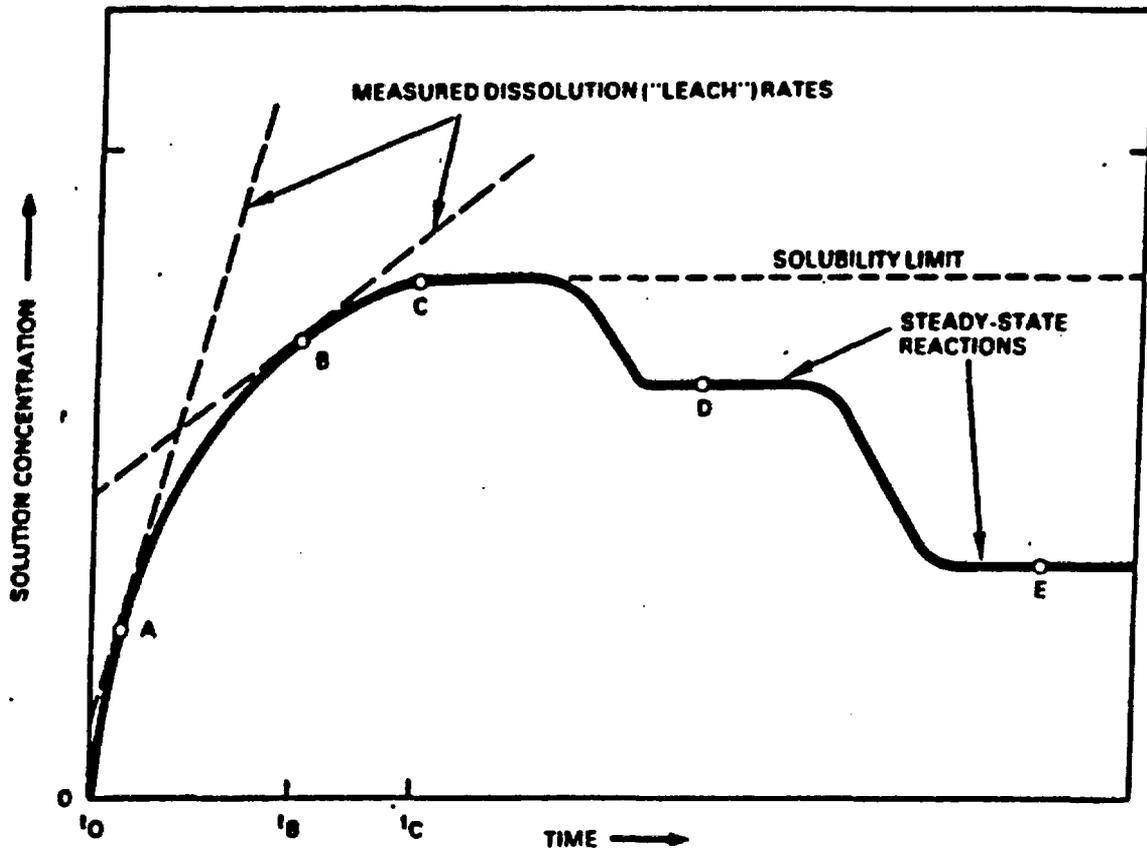


Fig. 1. Schematic illustration of solution concentration as a function of time for a hypothetical barrier materials + groundwater system.

Source: APTED 1982a. M. J. Apted, Overview of Hydrothermal Testing of Waste Package Barrier Materials by the Basalt Waste Isolation Project, RHO-BW-SA-228 P, Rockwell Hanford Operations, Richland, Washington, 1982.

it is evident that some steady states may develop as a result of conditions which are so special that they have little or no relevance to the physicochemical environments that are expected to develop in an NWRB during the post-containment period.

Third, the figure is misleading in that it implies that steady-state concentrations of radionuclides dissolved in groundwater in a closed isobaric, isothermal system must decrease with increased time. This is not necessarily so. A closed multi-solid-phase hydrothermal system will, with time (i.e., upon conversion of highly metastable to less metastable phase assemblages), evolve toward lower total free energy states, and the amounts of dissolved radionuclides may either decrease or increase depending on: (1) the values of radionuclide solid-phase/groundwater partition coefficients, and (2) the reactive surficial masses of the solid phases that are present. (For the sake of argument, it is assumed here that there are no major kinetic barriers to radionuclide "exchange" between groundwater and coexisting solid phases.) This argument holds regardless of whether radionuclide-bearing solids are: (1) precipitated phases in which one or more radionuclides are major components, or (2) secondary minerals (e.g., clay minerals and zeolites) that are present prior to, or form during, hydrothermal alteration, and which contain radionuclides as adsorbed, chemisorbed, or absorbed trace components. Experimental evidence that supports these statements includes the data that BWIP has obtained on the concentration-vs-time behavior of cesium in an experiment performed on the system simulated spent fuel + groundwater + basalt at 300°C. During this experiment — run BSF-3 described by Myers et al. (1983, Table A-8) — the

concentration of cesium, initially ~3 mg/L, increased sharply to ~48 mg/L after 1 h, then decreased erratically to ~11 mg/L after 571 h, and thereafter gradually rose to ~47 mg/L after 2875 h. Assuming that these results are not attributable to analytical error or the presence of large quantities of cesium-bearing colloids in the synthetic groundwaters, it is evident that, after initially reaching a "high" concentration due to relatively rapid dissolution of the waste form, it is not necessarily true that the solubility of a dissolved radionuclide will thereafter always either remain constant or continuously decrease with increasing time.

8. Some consequences of using different synthetic groundwaters and different analytical methods in barrier materials + groundwater experiments -

It is unfortunate that BWIP staff members and contractors have used so many different types of synthetic groundwaters in their hydrothermal experiments (e.g., see the analyses of synthetic groundwaters GR-3, GR-A, and GR-W listed in Table A.6 of Appendix A in this report). This is not to say necessarily that any of the experimental results were affected significantly by the use of a particular type of starting synthetic groundwater, but the possibility exists. It is also unfortunate that different analytical methods have been used to determine the compositions of synthetic groundwaters. Due to the significantly different accuracies of some of the analytical data, in certain specific instances it is very difficult to make valid comparisons between the results obtained for different waste form + groundwater ± basalt systems.

9. Some comments on measured and calculated values of pH for synthetic groundwaters — Calculations of pHs for synthetic groundwaters at high temperatures in the systems simulated spent fuel + groundwater and simulated spent fuel + groundwater + basalt described by Myers et al. (1983) are of questionable accuracy. Until there is some means of validating the accuracy of these calculated pHs, no particular significance should be lent to them. Also, because Myers et al. correctly state that high-temperature pHs in waste form + groundwater ± basalt systems cannot be inferred from pHs measured at 25°C, it is uncertain why these investigators have presented such lengthy discussions of observed variations in pH at 25°C.

4. PUBLISHED BWIP INFORMATION ON THE SOLUBILITIES OF RADIONUCLIDES AT 1 ATM 25 TO 90°C

4.1 BWIP APPROACH TO DATA DEVELOPMENT

According to Early et al. (1982) and Early et al. (1984), BWIP calculations of the solubilities of radionuclides at 1 atm, 25 to 90°C are partly based on the following premises:

1. "Baseline" calculations of the solubilities of radionuclides at 25°C can be performed using published thermodynamic data for aqueous radionuclide species and radionuclide-bearing solid phases. The results of these calculations — while only approximate due to a large number of associated uncertainties and potential sources of error — provide valuable preliminary indications of the nature of radionuclide solubility in basalt/groundwater systems. It is fully recognized that laboratory tests will be required to confirm the accuracy of the calculated solubilities.
2. The solubilities of radionuclides in the far field of an NWRB at the Hanford Site will be controlled primarily by chemical reactions that occur between groundwater and the solid phases (primary minerals, secondary minerals, and volcanic glass) in the basalts.
3. Because the solubilities of many radionuclides are influenced by the Eh, pH, and composition of groundwater, calculations of radionuclide solubilities should be performed using ranges of values for these geochemical properties which encompass the values that have been

measured or are expected to exist in the host rocks. This approach offers two advantages: (1) the sensitivity of radionuclide solubilities to Eh, pH, and groundwater chemistry can be evaluated, thus defining the degree to which these variables must be known in order to accurately predict the solubilities of radionuclides in basalt/groundwater systems; and (2) the results of solubility calculations can be used to identify the necessary geochemical conditions for experimental confirmation of calculated solubilities for key radionuclides.

The weight of the available evidence concerning Eh, pH, and solute chemistry of Grande Ronde groundwaters indicates that Eh and pH are fairly constant, but groundwater chemistry is rather variable.

Measured values of Eh for Grande Ronde groundwaters, which in many instances are of suspect accuracy, range from +0.35 to -0.2 V.

However, using thermodynamic data for (1) solute species that are abundant in Grande Ronde groundwaters, and (2) the principal minerals in Grande Ronde basalts, BWIP staff members have estimated that the Eh of groundwaters in Grande Ronde basalts is -0.40 ± 0.05 V at $57 \pm 2^\circ\text{C}$ (DOE 1982). Measured pH values for Grande Ronde groundwaters are very uniform, viz., 9.5 ± 0.9 . Finally, variations in the chemistry of Grande Ronde groundwaters are well known to BWIP geochemists through chemical analyses performed on 29 different samples of Grande Ronde groundwater obtained from five separate wells on the Hanford Reservation. [However, Early et al. (1984) do not give the ranges of concentration of principal solute species (Na^+ , Cl^- , F^- , SO_4^{2-} and SiO_2°) in these groundwaters, nor do they

indicate which reaction or reactions are most influential in establishing and maintaining the high pHs of the groundwaters.]

4. The presence of SO_4^{2-} in Grande Ronde groundwaters, and the evidence indicating relatively reducing (low Eh) conditions in the Grande Ronde Formation basalts, indicates that the potential effects of sulfate/sulfide equilibration should be explored in calculations of radionuclide speciation and solubility in Grande Ronde groundwaters. Although aqueous sulfide species (S^{2-} and HS^-) have not yet been detected in Grande Ronde groundwaters (GEPHART 1979) — either because Eh conditions are not sufficiently reducing to stabilize reduced aqueous sulfur species, or equilibrium is not achieved — it is important to consider the potential effects of the formation of these ions because: (1) they can be very important complexing agents for radionuclides such as Ni, Pd, Sb, and Pb; and (2) if they are present in significant amounts, they may induce precipitation of very insoluble Ni, Pd, Sb, and Pb sulfides which could control the solubilities of these radionuclides to very low values. For these reasons, it is useful to investigate how groundwater speciation and solubilities of radionuclides are affected by forming or not forming reduced aqueous sulfide species and solid sulfide precipitates.

4.2 REVIEW OF PUBLISHED BWIP SOLUBILITY INFORMATION

4.2.1 Experimental Results

There are no BWIP documents published as of July 1, 1984, which describe BWIP experiments on the solubilities of radionuclides at "low" temperatures (25 to 90°C). However, a limited quantity of solubility data obtained from BWIP sorption experiments are presented by Early et al. (1984, Table II) (see Table 1).

Table 1. Solubilities of radionuclides in natural and synthetic (GR-3) Grande Ronde groundwaters at 25°C and Eh = -0.3 V

Element/ radionuclide	Solubility-limiting solids and dominant aqueous species		Computed solubilities		
	Solubility- limiting solid	Dominant aqueous species	Solubility range in Grande Ronde groundwaters (mol/L)	Solubility in GR-3 synthetic Grande Ronde groundwater (mol/L)	Solubility estimates from experiments and natural Grande Ronde groundwaters (mol/L)
Ni	NiO	NiCO ₃ ⁰	4 x 10 ⁻⁵ - 3 x 10 ⁻³	2 x 10 ⁻⁴	>10 ^{-6a}
	Ni(CO ₃) ₂ ²				
Se	Se	NSe	1 x 10 ⁻⁸ - 5 x 10 ⁻⁷	6 x 10 ⁻⁸	~10 ^{-6b}
Zr	ZrSiO ₄	Zr(OH) ₅	1 x 10 ⁻¹⁰ - 2 x 10 ⁻⁸	2 x 10 ⁻⁹	
Pd	Pd	NiCO ₃ ⁰	2 x 10 ⁻¹² - 4 x 10 ⁻⁹	2 x 10 ⁻¹⁰	
Sn	SnO ₂	SnO(OH) ⁺	4 x 10 ⁻¹⁹ - 2 x 10 ⁻¹⁷	2 x 10 ⁻¹⁸	
		SnO(OH) ₂ ⁰ , Sn(OH) ₃			
Sb	Sb(OH) ₃	Sb(OH) ₃ ⁰	1 x 10 ⁻⁷ - 2 x 10 ⁻⁷	1 x 10 ⁻⁷	
Sm	Sm(OH) ₃	Sm(OH) ₃ ⁰ , Sm(OH) ₄	3 x 10 ⁻⁹ - 5 x 10 ⁻⁸	3 x 10 ⁻⁹	
		Sm(OH) ₃ ⁺³ , Sm(OH) ₂ ⁺			
Eu	Eu(OH) ₃	Eu(OH) ₄ ⁻ , Eu(OH) ₃ ⁰	7 x 10 ⁻⁹ - 7 x 10 ⁻⁷	3 x 10 ⁻⁸	>10 ^{-7a}
		EuCO ₃ ⁺ , Eu(OH) ₂ ⁺³			
Pb	Pb(OH) ₂	PbCO ₃ ⁰	8 x 10 ⁻¹⁵	8 x 10 ⁻¹⁵	<10 ^{-8b}
		Pb(CO ₃) ₂ ²⁻			
Th	ThO ₂	Th(OH) ₄ ⁰			
U	USiO ₄	U(OH) ₅	2 x 10 ⁻¹¹ - 2 x 10 ⁻⁹	2 x 10 ⁻¹⁰	>10 ^{-9a}
Np	NpO ₂	Np(OH) ₅	2 x 10 ⁻¹¹ - 7 x 10 ⁻¹⁰	1 x 10 ⁻¹⁰	10 ^{-6b}
Pu	PuO ₂	Pu(OH) ₅ ^{-c}	5 x 10 ⁻¹² - 1 x 10 ^{-6c}	8 x 10 ^{-10c}	
		PuCO ₃ ^{2+d}	4 x 10 ⁻¹⁴ - 2 x 10 ^{-12d}	3 x 10 ^{-10d}	
Am	Am(OH) ₃	Am(CO ₃) ₂ , Am(CO ₃) ₃ ³⁻	4 x 10 ⁻⁹ - 1 x 10 ⁻⁶	2 x 10 ⁻⁸	10 ⁻⁹ - 10 ^{-8e}
		AmCO ₃ ⁺			

^aFrom maximum concentration levels observed in Hanford groundwaters.

^bFrom sorption experiments.

^cSolubilities based upon published stability constant for PuCO₃²⁺ complex.

^dSolubilities based upon absence of PuCO₃²⁺ complex.

^eEdelstein et al. (1983).

Source: EARLY 1984. T. O. Early, G. K. Jacobs, and D. R. Dreves, "Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt," *Am. Chem. Soc. Symp. Ser.* 246, 147-166, Table II, 1984.

4.2.2 Calculational Results

Early et al. (1984) have calculated solubilities for radionuclides in Grande Ronde groundwaters at 25°C using: (1) ΔG_f° ,_{298K} data for aqueous species and solids, and (2) equilibrium constants ($\log K_{eq}$ values) for the reactions among the aqueous species and solid phases. Thermodynamic data for the calculations were obtained mainly from Rai and Serne (1978), Benson and Teague (1980), Phillips (1982), Rai et al. (1982), and Nair et al. (1982). Activity coefficients for aqueous species were calculated using the Guntelberg approximation (STUMM 1981). The major goals of the calculations were to determine how calculated radionuclide solubilities would be affected by: (1) variations in Eh and pH, (2) variations in Grande Ronde groundwater chemistry, and (3) constraints on aqueous sulfur species equilibrium.

The effects of Eh on calculated radionuclide solubilities were established by systematically varying values for this parameter in the calculations. The effects of variable groundwater pH and chemistry were determined by performing calculations for 29 different Grande Ronde Basalt groundwater compositions. The variability in groundwater pH and composition causes the calculated solubilities of many radionuclides to vary by two-to-three orders of magnitude. Because the calculations indicate that most of the dominant soluble species are either hydroxy or carbonate complexes, much of the variation in radionuclide solubilities is due, either directly or indirectly, to the different pHs of the groundwaters. Early et al. (1984) also state that

computed values of radionuclide solubilities did not seem to be significantly affected by different concentrations of F^- , Cl^- , SO_4^{2-} and SiO_2^0 in the groundwaters.

The effects of constraints on aqueous sulfur species equilibrium were tested using the GR-3 groundwater composition (JONES 1982).

Calculations were performed for key radionuclides as follows: (1) reduction of SO_4^{2-} to S^{2-} and/or HS^- was allowed to occur as Eh was lowered; and (2) sulfate reduction was prohibited (i.e., dissolved sulfur was only allowed to exist in the form of SO_4^{2-} ions, regardless of the imposed value of Eh). Results of the calculations indicate that Ni, Pd, Sb, and Pb are particularly sensitive to the presence of S^{2-} and HS^- in the groundwater; specifically, when significant amounts of these species are present, and at low values of Eh, the calculations suggest that solid sulfide phases will control the solubilities of Ni, Pd, Sb, and Pb.

Results of the solubility calculations performed by Early et al. (1984) are summarized in Table 1. The solubility values listed are partly based on the assumption that dissolved sulfur exists entirely as SO_4^{2-} in Grande Ronde groundwaters. (This restriction on the calculations was imposed because S^{2-} and HS^- have not yet been detected in Grande Ronde groundwaters.) The reference value of Eh for the calculations is -0.3 V. This value is approximately midway between the theoretical estimate of Eh for basalt/groundwater equilibrium (JACOBS 1981) and the average of measured values of Eh for Grande Ronde groundwaters. Table 1 also lists the solid phases that control solubility and the dominant dissolved species. Because it was assumed that dissolved

sulfur exists entirely as SO_4^{2-} , the possibility that calculated solubilities for Ni, Pd, Sb, and Pb might be controlled by sulfide solid phases was precluded. A limited number of solubility estimates obtained from analyses of Grande Ronde groundwaters and from recent sorption experiments are presented in the last column of Table 1. A comparison of these estimates with the calculated solubilities reveals significant discrepancies for many of the radionuclides.

Examination of the data presented in Table 1 leads to several significant conclusions (EARLY 1984). The dominant soluble radionuclide species are predicted to be hydroxy complexes (Zr, Pd, Sn, Sb, Sm, Eu, Th, U, Np, and Pu) and carbonate species (Ni, Sm, Eu, Pb, U, Np, Pu, and Am). The stabilities of these complexes are attributable to the high values of pH of Grande Ronde groundwaters and to the absence of significant quantities of other types of ligands that could potentially form strong complexes with many of the radionuclides. Solids that control solubility for the selected radionuclides include hydroxides and hydrous oxides (Pd, Sb, Sm, Eu, Pb, and Am), oxides (Ni, Sn, Th, Np, and Pu), pure elements (Se and Pd), and silicates (Zr and U). This rather narrow range of structural/chemical types of solid phases is attributable in large measure to the high pHs and (nominally) low Eh of the groundwater.

It is a well established fact that the solubilities of many radionuclides are affected significantly by changes in groundwater temperature. Early et al. (1984) attempted to determine the effects of increasing temperature from 25 to 60°C by calculating solubilities for uranium and plutonium in GR-3 groundwater using thermodynamic data given by Langmuir (1982)

and Lemire and Tremaine (1982). These calculations suggest that, at 60°C, the solubilities of uranium and plutonium are approximately 10 times greater than at 25°C. By analogy (because the required thermodynamic data are not available), Early et al. (1984) suggest that increasing temperature from 25 to 60°C will also result in modest increases in the solubilities of many other radionuclides.

4.3 BWIP-CITED LIMITATIONS OF THEIR SOLUBILITY INFORMATION

Early et al. (1982) and Early et al. (1984) cite the following important limitations of BWIP calculations of the solubilities of radionuclides at 1 atm, 25 to 90°C.

1. BWIP calculations of the stabilities of aqueous radionuclide species and coexisting radionuclide-bearing solid phases — which yield calculated solubilities for radionuclides — are valid in principle, but may not be directly applicable to "real" basalt/groundwater geochemical environments in an NWRB. The principal limitation of the calculations is the fact that existing data bases do not contain thermodynamic data for all of the radionuclide-bearing aqueous species and solid phases which can potentially exist in basalt/groundwater systems. An absence of thermodynamic data for solids that are more stable than those represented in the data base will result in calculated radionuclide solubilities that are erroneously high. On the other hand, if thermodynamic data are unavailable for aqueous complexes of radionuclides that are more stable than those represented in the data base, then calculated radionuclide solubilities are apt to be too low. In addition to these uncertainties,

there may be significant errors in some of the thermodynamic data that are currently being used to calculate solubilities for radionuclides. BWIP has made no attempt to critically evaluate the accuracy of available thermodynamic data, although comparisons among different compilations were made in an attempt to detect and eliminate erroneous data resulting from typographical errors. Also, BWIP has made no attempt to determine how calculated radionuclide solubilities are affected by statistically determined uncertainties for the thermodynamic data.

2. BWIP calculated solubilities for radionuclides are for 25°C, whereas measured temperatures of groundwaters in the Grande Ronde Basalt range from 49 to 58°C. The inability to perform accurate calculations for a 49 to 58°C temperature range is due to an absence of thermodynamic data (or a lack of accurate thermodynamic data) on pertinent homogeneous and heterogeneous equilibria at elevated temperatures. However, calculated radionuclide solubilities for 49 to 58°C should not be greatly different from those for 25°C; it is likely that raising temperature from 25 to ~60°C will lead to increases in the solubilities of most radionuclides, but these increases are not expected to be larger than one order of magnitude.
3. BWIP calculations are based on the assumption that the solubilities of radionuclides are controlled by the most stable solid phases of fixed composition. If, instead, the solubilities of radionuclides are controlled by metastable solid phases in the geochemical environments of an NWRB, then these solubilities would probably be

systematically higher than the solubilities predicted from thermodynamic calculations. Also, because BWIP solubility calculations are based on the assumption that solid phases (and particularly radionuclide-bearing solid phases) have fixed compositions, they cannot account for the potentially significant effects of solid solution. For example, rather than precipitating separately as discrete "pure" solid phases, the rare earth elements europium and samarium may coprecipitate as an hydroxide solid solution.

Similarly, one or more actinide elements and zirconium may coprecipitate in a single solid solution phase (an oxide or hydroxide solid solution). Moreover, a radionuclide-rich solid solution phase may precipitate even if there are more stable "pure" solid phases for one or more of the radionuclides. Coprecipitation tends to raise the observed solubilities of those radionuclides for which more stable solid phases exist.

4. The potentially significant effects of organic complexing agents have not been taken into account in BWIP calculations of the groundwater solubilities of radionuclides.

4.4 ASSESSMENT OF BWIP SOLUBILITY INFORMATION

Judging from the discussions presented in Early et al. (1984), BWIP is well aware of the limitations of its information on the solubilities of radionuclides in Grande Ronde groundwaters at "low" temperatures (25 to 90°C). Nevertheless, a few key points regarding this information merit further discussion, and several specific comments concerning the calculations performed by Early et al. are apropos.

1. The use of calculated radionuclide solubilities to estimate radionuclide source terms. Several important conclusions can be drawn from a comparison of calculated radionuclide solubilities and measured radionuclide (or radionuclide-analog element) solubilities. Calculated groundwater solubilities of radionuclides at "low" temperatures are frequently many orders of magnitude lower than corresponding measured solubilities obtained from hydrothermal experiments performed at "high" temperatures. The indication that the solubilities of radionuclides are greater at high temperatures is not surprising, but the fact that these solubilities are in some cases many orders of magnitude greater at high temperatures suggests that calculated solubilities may be unrealistically low and, therefore, nonconservative. According to Early et al. (1984), one of the reasons that calculated solubilities probably represent minimum values for the steady-state concentrations of radionuclides in groundwater is that the solid phases which control solubilities in the thermodynamic calculations are seldom found as secondary phases in hydrothermal experiments; specifically the results of hydrothermal experiments indicate that radionuclide solubilities are often controlled by metastable radionuclide-rich solid phases for which there are no available thermodynamic data. For this reason, in order to be conservative, it may be advisable to treat radionuclide solubilities calculated from thermodynamic data as minimum values of the solubilities which are suitable for estimating radionuclide source terms for an NWRB.

2. Lack of information on the solubilities of radionuclides at "low" temperatures. Unfortunately, there is very little available information on the experiments that BWIP staff members and/or contractors have per-

formed on the solubilities of radionuclides at 25 to 90°C. A small amount of data obtained from these experiments has been presented by Early et al. (1984, Table II).

3. Treating Eh as an independent variable. In the radionuclide solubility calculations performed by Early et al. (1982) and Early et al. (1984), Eh is treated as an independent variable, which is generally not the case in natural and synthetic rock/groundwater systems. Rather, in these systems, which are typically rock dominated, Eh is a dependent variable with a value that is either determined by, or strongly influenced by, the effective bulk composition, temperature, and reaction kinetics of the rock/groundwater system.

4. Results of recent calculations of the solubilities of uranium and nickel. Recent calculations of the solubilities of uranium and nickel in synthetic Grande Ronde groundwater GR-3 at 25 and 60°C and Eh = -0.3 V using the computer code MINTEQ yield results that are significantly different from those obtained by Early et al. (1982) and Early et al. (1984) (G. K. Jacobs, personal communication).

● Uranium. The calculations performed with MINTEQ indicate that UO_2 , with a solubility of 10^{-8} mol/L, is the most stable uranium-bearing solid phase. By contrast, the calculations performed by Early et al. indicate that USiO_4 , with a solubility of $10^{-9.96}$ mol/L, is the most stable uranium-bearing solid phase. These inconsistent results are attributable to the use of different formation constants ($\log K_f$ values) for USiO_4 . In the MINTEQ data base, $\log K_f = 7.62$ for USiO_4 , whereas in the data base employed by Early et al., $\log K_f = 9.07$. The value in the MINTEQ data

base is probably more accurate, judging from the results obtained in a recent validation study of the thermodynamic data for uranium in the MINTEQ data base (KRUPKA 1983).

● Nickel. Assuming no SO_4^{2-} speciation (reduction) to S^{2-} and HS^- ions, the calculations performed with MINTEQ indicate that $\text{Ni}(\text{OH})_2$, with a solubility of 2.8×10^{-6} mol/L, is the most stable nickel-bearing solid phase. By contrast, the calculations performed by Early et al. indicate that NiO , with a solubility of 1.8×10^{-4} mol/L, is the most stable nickel-bearing solid phase. These inconsistent results are attributable to the use of different formation constants for $\text{Ni}(\text{OH})_2$. In the MINTEQ data base, $\log K_f = -10.8$ for $\text{Ni}(\text{OH})_2$, whereas in the data base employed by Early et al., $\log K_f = -12.7$ (BENSON 1980). When sulfate speciation to S^{2-} and HS^- ions is permitted in the calculations, the calculations performed with MINTEQ again indicate that $\text{Ni}(\text{OH})_2$ is the most stable solid phase, and its calculated solubility is 2.8×10^{-6} mol/L. By contrast, calculations performed by Early et al. indicate that NiS , with a solubility of 1.8×10^{-4} mol/L, is the most stable nickel-bearing solid phase. The different results are attributable to the different values of $\log K_f$ for NiS in the data bases that were used to perform the two sets of calculations; in the MINTEQ data base, $\log K_f = 41.7$, while in the data base used by Early et al., $\log K_f = 47.3$.

5. ADEQUACY OF RADIONUCLIDE SOLUBILITY INFORMATION FOR
THE HANFORD, WASHINGTON, CANDIDATE HLW REPOSITORY SITE

The text below contains item-by-item discussions of the principal apparent inadequacies of radionuclide solubility information that has been developed for, or pertains to, the Hanford, Washington, candidate HLW repository site.

1. The available radionuclide solubility information is of uncertain relevancy to repository licensing requirements because it remains to be determined what solubility information will be needed to conduct defensible performance-assessment analyses and to satisfy the technical criteria and "reasonable assurance" requirement of 10 CFR 60.

Published BWIP reports do not describe specific plans for solubility data utilization in waste-package and site-performance assessments. A trend toward acquiring experimental data (as opposed to calculational data) for "key" hazardous radionuclides and using conservative estimates of "real" solubilities in performance-assessment calculations is evident, but approaches to be taken in using solubility data in performance assessments are not discussed in detail. By analyzing the results of performance-assessment calculations using available radionuclide solubility data, it should be possible to identify specific solubility information which will be needed for licensing of an NWRB at the Hanford Site. It can be expected that the results of the calculations will also be useful in determining how much emphasis should be given to solubility studies vis-á-vis studies of other geochemical barriers (e.g., sorption) in BWIP's data-development activities relating to radionuclide mobilization, transport, and release.

2. BWIP theoretical treatment of the solubility-vs-time behavior of radionuclides in barrier materials + groundwater systems is not supported by fundamental thermodynamic theory and pertinent experimental data.

BWIP theoretical treatment of the solubility-vs-time behavior of radionuclides in closed, isobaric, isothermal barrier materials + groundwater systems implies that, after reaching high initial concentrations due to rapid dissolution of the waste form, the amounts of radionuclides dissolved in groundwater will thereafter always either remain constant or decrease with increasing time. This is not necessarily so, as is evident from both fundamental thermodynamic theory and selected pertinent high-temperature solubility data obtained by BWIP staff and contractors. A closed multi-solid-phase hydrothermal system will, with time (i.e., upon conversion of highly metastable to less metastable phase assemblages), evolve toward lower total free energy states, and the amounts of dissolved radionuclides may either decrease or increase depending on (1) the values of radionuclide solid phase/groundwater partition coefficients, and (2) the reactive surficial masses of the solid phases that are present. This is true regardless of whether radionuclide-bearing solids are: (1) precipitated phases in which one or more radionuclides are major components, or (2) secondary minerals (e.g., clay minerals and zeolites) that are present prior to, or form during, hydrothermal alteration, and which contain radionuclides as adsorbed, chemisorbed, or absorbed trace components. Experimental evidence that supports these statements includes the data that BWIP has obtained on the concentration vs time behavior

of cesium in an experiment performed on the system simulated spent fuel + groundwater + basalt at 300°C. During this experiment — run BSF-3 described by Myers et al. (1983, Table A-8) — the concentration of cesium, initially ~3 mg/L, increased sharply to ~48 mg/L after 1 h, then decreased erratically to ~11 mg/L after 571 h, and thereafter rose to ~47 mg/L after 2875 h. Assuming that these results are not attributable to analytical error or the presence of large quantities of cesium-bearing colloids in the synthetic groundwaters, it is evident that, after initially reaching a comparatively high concentration due to relatively rapid dissolution of the waste form, it is not necessarily true that the solubility of a dissolved radionuclide will thereafter always either remain constant or decrease with increasing time.

3. Experimental data on the solubilities of radionuclides in barrier materials + groundwater systems are sparse and were obtained under experimental conditions which do not adequately simulate the chemical conditions that are expected to prevail in the vicinity of waste packages after repository closure and groundwater resaturation.

BWIP staff members and contractors have performed only a small number of experiments on the solubilities of radionuclides in barrier materials + groundwater systems, and all of the systems investigated to date are waste form + groundwater ± basalt systems. One of the principal deficiencies of these studies is the failure to adequately investigate the effects of waste form composition on experimental results; specifically, it is possible that the solubilities/concentrations of some radionuclides may be significantly affected by relatively small changes in the chemical

composition of the waste form. Furthermore, the use of freshly crushed basalt as a solid starting material in barrier materials + groundwater experiments systems is inappropriate because the crushed basalt in the packing material of waste packages of an NWRB would probably be partly to mostly altered to secondary minerals by the end of the containment period. The data obtained from barrier materials + groundwater experiments also indicate that results are partly dependent on the physical states of the solid starting materials (especially the grain sizes of these materials). Still another major deficiency of experimental studies of barrier materials + groundwater systems is that canister materials and fully radioactive waste forms have not yet been included among the solid starting materials for experiments. Experiments on systems which include these materials will more accurately simulate the chemical environments near the waste packages in an NWRB after the containment period. Also, experiments on fully radioactive waste forms will provide some of the data that are needed to determine whether or not radionuclide solubilities are strongly affected by radiolytic alteration of solid materials and/or radiolysis reactions in groundwater.

4. Experimental data on the solubilities of radionuclides in basalt/groundwater systems at "low" temperatures (25 to 90°C) are very sparse.

Experimental data on the solubilities of radionuclides at low temperatures (25 to 90°C) are needed to determine the extent to which solubility restricts radionuclide mobility in the far field of an NWRB at the Hanford Site. Solubility measurements are especially needed for those radionuclides which (1) have comparatively high solubilities in

Grande Ronde groundwaters at 25 to 90°C, and (2) are not readily sorbed by the primary and secondary minerals in Hanford-Site basalts and interbed rocks.

5. Researchers concerned with acquiring and publishing experimental data on the solubilities/concentrations of radionuclides in waste form + groundwater ± basalt systems have not yet developed appropriate methods for calculating or estimating the precision of their data.

In view of the "reasonable assurance" requirement of NRC regulation 10 CFR 60, it seems likely that, at the very least, it will be necessary to determine the precision of solubility data for radionuclides which are high (considered to be very hazardous) in a final ranking of hazardous radionuclides.

6. Successful implementation of a "fate of radionuclides" approach to barrier materials + groundwater experimentation requires unequivocal identification of all of the major sorption/precipitation sites of radionuclides in the solid reaction products of hydrothermal experiments.

BWIP's "fate of radionuclides" approach to barrier materials + groundwater experimentation is a useful strategy for obtaining data that are needed for successful predictive performance-assessment modeling of the release and transport of radionuclides in an NWRB. However, successful implementation of this approach requires unequivocal identification of all of the major "sites" (locations) of radionuclides in the solid reaction products of hydrothermal experiments. These sites include not only precipitated, radionuclide-rich solid phases, but also primary minerals

and secondary minerals/solid phases which contain adsorbed, chemisorbed, and/or absorbed radionuclides. The task of identifying these solids is made difficult by the fact that, in most experiments, there will be only small amounts of radionuclides present in the solid reaction products: evidently, this is the principal reason why, to date, BWIP has had only minimal success in identifying and characterizing the radionuclide-bearing solid phases in their experimental run products.

6. RECOMMENDATIONS

An evaluation of the information on radionuclide solubility that is pertinent to the Hanford, Washington, candidate HLW repository site indicates that there are six principal areas of technical investigation which should receive further attention to ensure continued progress in acquiring radionuclide-solubility information that relates to repository licensing activities:

1. To date, BWIP staff members and contractors have tested only four different simulated waste forms (one simulated spent fuel and three simulated HLW borosilicate glasses) in their "high-temperature" (90 to 300°C) hydrothermal experiments on waste form + groundwater ± basalt systems. Additional experiments with other similar but different waste forms are needed to test the effects of slight changes in the composition of the waste form. It is possible that the solubilities/concentrations of some radionuclides may be altered significantly by relatively small changes in the composition of the waste form.
2. BWIP investigations of barrier materials + groundwater systems should include experiments in which hydrothermally altered basalt + bentonite mixtures (75% basalt + 25% bentonite) and pieces (not powders) of simulated canister and cladding material are among the solid starting materials. (The use of powdered simulated canister and cladding material in the experiments would not be appropriate because canister and cladding material will not be present as powders in the waste packages of an NWRB.) Experiments on systems that include these materials

will more accurately simulate the geochemical environments in the vicinity of the waste packages in an NWRB after the containment period (nominally, 300 to 1000 years after repository closure). A principal goal of these experiments should be to determine whether or not canister metal lowers redox conditions to a point that the solubilities of certain key multivalent-state radionuclides (e.g., ^{99}Tc , ^{237}Np , and ^{79}Se) are significantly decreased.

3. BWIP investigations of barrier materials + groundwater systems should include experiments on fully radioactive waste forms because the results of these experiments will provide some of the data that are needed to determine whether or not radionuclide solubilities are strongly affected by radiolysis reactions. Recent experiments performed by Gray (1984) indicate that radiolysis reactions in methane-bearing groundwaters can produce significant quantities of polyethylene-like hydrocarbons. Obviously, follow-up experiments are needed to investigate the possibility that the presence of these hydrocarbons can have a significant effect on the solubilities of radionuclides in Grande Ronde groundwaters.

4. Additional experimental data are needed for those radionuclides which have comparatively high solubilities in basalt/groundwater systems at 25 to 90°C. Evidently, BWIP has already performed a significant number of solubility experiments at 25°C, because some selected preliminary results are presented by Early et al. (1984, Table II), and these investigators note that Salter and Ames (1982) have described an experimental method that appears to be suitable for measuring the solubilities of radionuclides at low temperatures.

5. BWIP reports containing radionuclide solubility data do not present calculated or estimated limits of error for the data. This omission is unfortunate, because it is difficult to assess the significance of radionuclide solubility data when the precision of the data is unknown. Therefore, the BWIP staff should begin to develop appropriate methods for estimating the precision of their radionuclide solubility data.

6. BWIP staff members and contractors should be aware that it is possible to determine the accuracies of radionuclide solubilities/ concentrations acquired from experiments with Dickson-type apparatus by obtaining "reversals" for the data. These reversals, which involve approaching apparent steady-state conditions from both oversaturation and undersaturation during experimentation, are achieved in the following way. First, in order to approach radionuclide solubility/ concentration levels from oversaturation, a radionuclide-rich fluid is injected into the gold or teflon bag in the pressure vessel. This injection should cause the fluid to become supersaturated with radionuclides, so if the concentrations of radionuclides measured prior to the injection event actually represent "true" solubilities, then sorption/precipitation of radionuclides should begin to occur, thus causing radionuclide concentrations to decrease toward their former levels. Conversely, in order to approach solubility/concentration levels from undersaturation, an appropriate quantity of non-radionuclide-bearing synthetic groundwater can be injected into the gold or teflon bag in the pressure vessel, thereby diluting the nominally radionuclide-saturated synthetic groundwater in the pressure vessel. This mixing should induce partial dissolution of radionuclide-rich solid

phases (if they are present), and/or result in "release" of sorbed radionuclides to the groundwater, and, therefore, the concentrations of radionuclides should begin to return to their original values.

Following these two procedures for reversing (bracketing) measured concentrations of radionuclides, it is possible to obtain ranges of radionuclide concentration which encompass the "true" steady-state concentrations (solubilities) of the radionuclides.

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APPENDIX A

CHEMICAL COMPOSITIONS OF SOLID AND FLUID STARTING MATERIALS FOR "HIGH-TEMPERATURE" (90 TO 300°C) HYDROTHERMAL EXPERIMENTS ON WASTE FORM + GROUNDWATER ± BASALT SYSTEMS

This appendix contains Tables A.1-A.6, which list the chemical compositions of the solid and fluid starting materials that BWIP staff members and contractors have used in "high-temperature" (90 to 300°C) hydrothermal experiments on waste form + groundwater ± basalt systems.

Table A.1. Chemical composition of simulated spent fuel^a

Component	Wt %	Component	Wt %
UO ₂	96.09	Te	0.05
ThO ₂	0.95	Sr	0.07
Y ₂ O ₃	0.05	Ba	0.15
CeO ₂	0.26	Pr	0.10
Mo	0.30	Sm	0.56
Pd	0.30	Zr	0.32
Cs	0.26	Re	0.13
I	0.02		

^aComposition from Woodley et al. (1981).

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 3.7, September 1983.

Table A.2. Chemical composition of simulated CHLW borosilicate glass^a

Component	Amount (Wt %)	Component	Amount (Wt %)
SiO ₂	39.80	La ₂ O ₃	0.56
Na ₂ O	12.80	PdO	0.56
Fe ₂ O ₃	10.34	P ₂ O ₅	0.51
B ₂ O ₃	9.47	Cr ₂ O ₃	0.44
ZnO	4.97	SrO	0.40
Nd ₂ O ₃	4.67	Sm ₂ O ₃	0.35
TiO ₂	2.97	TeO ₂	0.28
MoO ₃	2.42	Y ₂ O ₃	0.23
CaO	2.00	NiO	0.21
ZrO ₃	1.88	Rh ₂ O	0.18
CeO ₂	1.26	Rb ₂ O	0.18
RuO ₂	1.13	Eu ₂ O ₃	0.08
Cs ₂ O	1.09	Gd ₂ O ₃	0.05
BaO	0.59	CdO	0.04
Pr ₆ O ₁₁	0.56	Ag ₂ O	0.03

^aPacific Northwest Laboratory (PNL) 76-68 Composition (MCVAY 1983).

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer,
Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials
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 SD-BWI-TI-141, Rev. 0-0, Table 3.4, September 1983.

Table A.3. Chemical composition of radionuclide-doped simulated CHLW borosilicate glass^a

Component	Wt %	Component	Wt %
SiO ₂	40.0	La ₂ O ₃	0.53
Na ₂ O	12.5	Pr ₆ O ₁₁	0.53
Fe ₂ O ₃	9.6	P ₂ O ₅	0.46
B ₂ O ₃	9.5	Cr ₂ O ₃	0.40
ZnO	5.0	SrO	0.37
UO ₂	4.2	Sm ₂ O ₃	0.32
TiO ₂	3.0	TeO ₂	0.26
MoO ₃	2.2	Y ₂ O ₃	0.21
CaO	2.0	NiO	0.20
ZrO ₂	1.7	Rh ₂ O ₃	0.17
Nd ₂ O ₃	1.65	Rb ₂ O	0.13
CeO ₂	1.19	Eu ₂ O ₃	0.070
RuO ₂	1.07	Gd ₂ O ₃	0.050
CsO ₂	1.03	CdO	0.033
BaO	0.56	Ag ₂ O	0.031
PdO	0.53		

^aComposition from Bradley et al. (1979).

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 3.5, September 1983.

Table A.4. Chemical composition of simulated DHLW borosilicate glass^a

Component	Wt %	Component	Wt %
SiO ₂	41.83	Fe ₂ O ₃	13.65
Na ₂ O	12.43	MnO ₂	3.93
B ₂ O ₃	10.32	Zeolite ^b	2.94
TiO ₂	0.70	Al ₂ O ₃	2.74
Li ₂ O	4.00	NiO	1.53
MgO	1.40	Na ₂ CO ₃	1.18
ZrO ₂	0.35	CaO	1.01
La ₂ O ₃	0.35	Coal	0.66
		Na ₂ SO ₄	0.17
		CsNO ₃	0.15
		Sr(NO ₃) ₂	0.15

^aSavannah River Laboratory Type 131/TDS Waste Glass Composition.

^bLinde AW-500 Zeolite (Calcium-Aluminum-Silicate).

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 3.6, September 1983.

Table A.5. Chemical composition of grande ronde basalt sample RUE-1

Component	Wt %	Estimated (Wt %) uncertainty
SiO ₂	55.59	0.88
TiO ₂	2.21	0.04
Al ₂ O ₃	13.71	0.27
Fe ₂ O ₃	3.68	0.07
FeO	10.24	0.25
MnO	0.24	0.02
MgO	3.79	0.26
CaO	7.31	0.11
Na ₂ O	2.95	0.29
K ₂ O	1.63	0.06
P ₂ O ₅	0.35	0.02
Modal mineralogy		
Plagioclase (An ₄₀)		28.7
Pyroxene		17.1
Mesostasis		47.7
Titaniferous magnetite		5.12
Chlorophaeite		<u>1.65</u>
		100.27

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 3.1, September 1983.

Table A.6. Chemical compositions of synthetic groundwaters used in high-temperature hydrothermal experiments

Dissolved constituent	Concentrations in mg/L		
	GR-A ^a	GR-3 ^b	GR-WC
Na ⁺	250	358	410
K ⁺	1.9	3.4	<6
Ca ²⁺	1.3	2.8	2.52
Mg ²⁺	0.04	0.032	0.032
Cl ⁻	148	312	366
CO ₃ ²⁻	30	12.9	ND
HCO ₃ ⁻	36	42.9	ND
F ⁻	37	33.4	35.4
SO ₄ ²⁻	108	173	172
SiO ₂	86.6	76.2	74.9
pH	10.2	9.9	9.74

^aData from Holloway (1981).

^bData from Smith (1981).

^cData from Coles and Apted (1983) and Coles (1983).

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 3.2, September 1983.

APPENDIX B

SUMMARIES AND INTERPRETATIONS OF RESULTS OBTAINED FROM EXPERIMENTS PERFORMED ON WASTE FORM + GROUNDWATER ± BASALT SYSTEMS AT 10 TO 30 MPa, 90 TO 300°C

This appendix describes the "high-temperature" (90 to 300°C) experimental data that BWIP staff members and contractors have obtained on various waste form + groundwater ± basalt systems. The accounts and opinions provided are those of the writer, who is solely responsible for their clarity and accuracy.

Summaries and interpretations of the results of BWIP hydrothermal experiments are presented below for each system that has been investigated. The data described for each system are selected data which have been obtained from "typical" experiments — that is, one "typical" experiment for each temperature that has been investigated. All of the data listed or cited were obtained from Apted and Myers (1982), Myers et al. (1983), and Coles (1983b). These investigators do not list statistically determined or empirically estimated uncertainties for their data, so no attempt has been made here to account for the potential effects of such uncertainties. Consequently, interpretations of the trends of changes in groundwater composition (including changes in the concentrations of radionuclides and/or radionuclide-analog elements) during a given experiment are frequently very subjective.

In describing changes in groundwater composition during "typical" BWIP experiments, attempts have been made to correctly identify groundwater solute elements/species that exhibited steady-state (constant concentration vs time) behavior either briefly or continuously during each

of the experiments. These determinations are particularly important for radionuclides and radionuclide-analog elements in the groundwaters because, presumably, BWIP plans to use experimentally determined steady-state concentrations of these nuclides in their NWRB performance-assessment analyses. For comparison with some of the conclusions drawn here concerning whether or not radionuclide-analog elements exhibited steady-state behavior under a given set of experimental conditions (system, pressure, and temperature) — and if so, at what levels of concentration steady-state behavior was exhibited — this appendix also includes Tables B.1-B.5, which present corresponding conclusions drawn by Myers et al. (1983). Comparing the interpretations given in this report and those presented by Myers et al., it is evident that there are significant differences of opinion in many particular instances. These discrepancies are partly attributable to difficulties in interpreting the trends of concentration-vs-time data that frequently exhibit significant scatter. Finally, the summaries of selected BWIP experimental results presented here include listings of the secondary minerals/solid phases that formed during the experiments. The source of this information is Table 6.2 in Myers et al. (1983).

B.1 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED SPENT FUEL + GROUNDWATER

Experiments on this system were performed by BWIP staff members and are described by Apted and Myers (1982) and Myers et al. (1983).

B.1.1 Starting Materials

Starting materials were simulated spent fuel (Appendix A, Table A.1) and GR-3 synthetic groundwater (Appendix A, Table A.6) in a 1:10 ratio.

B.1.2 Experimental Conditions

Experiments were performed at 30 MPa and 100°C (run D6-8), 200°C (run D6-1), and 300°C (run D5-1) for 866 h, 690 h, and 2514 h, respectively.

B.1.3 Changes in Groundwater Composition

Measured changes in the compositions of groundwaters at 100, 200, and 300°C are as follows [see Myers et al. (1983, Tables A-2, A-3, and A-4)].

B.1.3.1 100°C (run D6-8)

The concentration of sodium, initially ~420 mg/L, decreased slightly throughout the experiment, reaching 378 mg/L after 714 h. The concentration of silicon, initially ~34 mg/L, decreased slightly throughout the experiment, reaching ~27 mg/L after 714 h. The concentration of SO_4^{2-} , initially ~34 mg/L, remained essentially constant for 19 h, then decreased to 27 mg/L after 161 h, and thereafter decreased to an apparent steady-state concentration of ~15 mg/L.

B.1.3.2 200°C (run D6-1)

The concentration of sodium, initially 355 mg/L (APTED 1982b), increased to 380 mg/L after 1 h and thereafter remained essentially constant. The

concentration of silicon, initially 33 mg/L (APTED 1982b), increased steadily to ~59 mg/L after 48 h, and thereafter slowly decreased, reaching a concentration of 51 mg/L after 532 h. The concentration of SO_4^{2-} , initially 172 mg/L (APTED 1982b), decreased more or less steadily to an apparent steady-state concentration of ~90 mg/L after 20 h.

B.1.3.3 300°C (run D5-1)

The concentration of sodium, initially 381 mg/L (MYERS 1983), remained nearly constant during the experiment. The concentration of silicon, initially ~32 mg/L (MYERS 1983), increased steadily to ~46 mg/L after 68 h, remained essentially constant through 334 h, and then declined to ~37 mg/L after 717 h. The concentration of SO_4^{2-} , initially 35 mg/L (MYERS 1983), decreased rapidly to an apparent steady-state concentration of ~13 mg/L after just 1 h.

B.1.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains of spent fuel that exhibited little evidence of alteration during experimentation.

The secondary minerals/solid phases that formed at 100, 200, and 300°C are as follows.

100°C (run D6-8): none detected.

200°C (run D6-1): none detected.

300°C (run D5-1): none detected.

B.1.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 100, 200, and 300°C are as follows [see pertinent run tables in Myers et al. (1983, Tables A-2, A-3, and A-4), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1983, Table 8.2) which are summarized in Table B.1].

B.1.5.1 100°C (run D6-8)

The concentration of molybdenum, initially 0 mg/L, increased sharply to ~53 mg/L after 1 h, then increased more or less steadily to an apparent steady-state concentration of ~80 mg/L after 161 h. The concentration of barium, initially ~0.9 mg/L, decreased to an apparent steady-state concentration of ~0.3 mg/L after 161 h. The concentration of strontium, initially ~0.164 mg/L, decreased more or less steadily to ~0.05 mg/L after 714 h.

B.1.5.2 200°C (run D6-1)

The concentration of molybdenum, initially ~0 mg/L (APTED 1982b), increased sharply to a concentration of ~60 mg/L after 1 h, and after 20 h it reached an apparent steady-state concentration of ~68 mg/L. The concentration of barium, initially 0.001 mg/L (APTED 1982b), increased to an apparent steady-state concentration of ~0.25 mg/L after 1 h, remained essentially constant through 20 h, and thereafter decreased slowly to another apparent steady-state concentration of 0.12 mg/L after 312 h. There are no available data for strontium.

B.1.5.3 300°C (run D5-1)

The concentration of molybdenum, initially ~2 mg/L (MYERS 1983), increased sharply to 100 mg/L after 1 h, then increased to an apparent steady-state concentration of ~152 mg/L after 68 h, and then decreased from 154 mg/L at 334 h to 136 mg/L after 717 h. The concentration of barium, initially 0.302 mg/L (MYERS 1983), decreased sharply to an apparent steady-state concentration of ~0.1 mg/L after 4 h, remained essentially constant through 182 h, and thereafter decreased to a new apparent steady-state concentration of ~0.05 mg/L. The concentration of strontium, initially 0.089 mg/L (MYERS 1983), remained essentially constant throughout the experiment.

B.2 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED SPENT FUEL + GROUNDWATER + BASALT

Experiments on this system were performed by geochemists at Temple University and are described by Apted and Myers (1982) and Myers et al. (1983).

B.2.1 Starting Materials

Starting materials were simulated spent fuel (Appendix A, Table A.1), Umtanum basalt (Appendix A, Table A.5), and GR-3 synthetic groundwater (Appendix A, Table A.6) in a 1:1:20 ratio.

B.2.2 Experimental Conditions

Experiments were performed at 30 MPa and 100°C (run BSF-4), 200°C (run BSF-2), and 300°C (run BSF-3) for 6143 h, 2014 h, and 2875 h, respectively.

B.2.3 Changes in Groundwater Composition

Measured changes in the compositions of groundwaters at 100, 200, and 300°C are as follows [see Myers et al. (1983, Tables A-5, A-6, and A-8)].

B.2.3.1 100°C (run BSF-4)

The concentration of sodium, initially 353 mg/L, remained more or less constant during the experiment. The concentration of silicon, initially 34.6 mg/L, increased sharply to 84.1 mg/L after 1 h, and thereafter remained more or less constant. The concentration of SO_4^{2-} , initially 172 mg/L, at first rose slightly to 186 mg/L after 52 h and thereafter decreased to an apparent steady-state concentration of ~125 mg/L after 642 h.

B.2.3.2 200°C (run BSF-2)

The concentration of sodium, initially 358 mg/L, decreased to an apparent steady-state concentration of 275-300 mg/L after just 1 h and then after 1197 h it apparently decreased from ~300 mg/L to 239 mg/L after 2014 h. The concentration of silicon, initially 35.5 mg/L, increased sharply to 173 mg/L after 1 h, increased erratically to 241 mg/L after 164 h, then rose sharply to an apparent steady-state concentration of ~350 mg/L after 357 h. The concentration of SO_4^{2-} , initially 190 mg/L, decreased slightly to an apparent steady-state concentration of 170 mg/L after 20 h, remained more or less constant through 1197 h, and then decreased to 138 mg/L after 2014 h.

B.2.3.3 300°C (run BSF-3)

The concentration of sodium, initially 353 mg/L, decreased sharply to 264 mg/L after 3 h and then rose to an apparent steady-state concentration of ~300 mg/L after 19 h. The concentration of silicon, initially 43 mg/L, increased sharply to ~207 mg/L after 1 h, then continued to rise more or less steadily to ~836 mg/L after 1075 h, and thereafter decreased to an apparent steady-state concentration of ~580 mg/L after 1891 h. The concentration of SO_4^{2-} , initially 204 mg/L, decreased to an apparent steady-state concentration of ~130 mg/L after 1 h, remained nearly constant through 42 h, and thereafter increased erratically to a maximum of 224 mg/L after 2875 h.

B.2.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains. Grains of spent fuel and the primary basalt minerals exhibited little or no evidence of alteration and appeared to be present in original amounts. By contrast, the surfaces of grains of the glass-rich basalt mesostasis were etched and pitted, indicating partial and uneven dissolution.

The secondary minerals/solid phases that formed at 100, 200, and 300°C are as follows.

100°C (run BSF-4): none detected.

200°C (run BSF-2): smectite, illite, heulandite, coffinite, uranium-oxide or hydroxide, and a cesium-bearing phyllosilicate.

300°C (run BSF-3): smectite, illite, K-feldspar, silica, weeksite or boltwoodite, coffinite, cesium-bearing phyllosilicate, scapolite, powellite-scheelite, palladium sulfide, and heulandite.

The silica formed in run BSF-3 exhibited poorly developed crystal faces, indicating that it was crystalline. Also, the weeksite and/or boltwoodite (K-U-silicates) occurred as blocky crystals on the grains of spent fuel. Discrete molybdenum- and/or cesium-rich phases were not observed, indicating either that they were present in only trace amounts or that molybdenum and cesium occurred principally as trace components in the crystal structures of secondary minerals.

B.2.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 100, 200, and 300°C are as follows [see pertinent run tables in Myers et al. (1983, Tables A-5, A-6, and A-8), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1983, Table 8.2) which are summarized in Table B.2].

B.2.5.1 100°C (run BSF-4)

The concentration of molybdenum, initially ~0.2 mg/L, rose rapidly to 46.6 mg/L after 1 h, remained essentially constant through 52 h, and then gradually increased to an apparent steady-state concentration of ~75 mg/L after 642 h. The concentration of barium, initially 1.5 mg/L, varied erratically between 0 and 3.5 mg/L during the experiment. The concentration of strontium, initially 0.21 mg/L, rose rapidly to 11 mg/L after 1 h and thereafter decreased to an apparent steady-state concentration of ~0.2 mg/L (the initial concentration) after 307 h. The concentration of cesium, initially 3.4 mg/L, rose sharply to an apparent

steady-state concentration of ~50 mg/L after just 1 h. The concentration of iodine, initially 0 mg/L, increased to an apparent inventory-limited concentration of ~11 mg/L after just 1 h. The concentration of uranium, initially 0 mg/L, rose rapidly to 1.16 mg/L after 1 h, decreased to 0.49 mg/L after 18 h, and then decreased from 0.49 mg/L after 52 h to an apparent steady-state concentration of ~0.3 mg/L after 139 h.

B.2.5.2 200°C (run BSF-2)

The concentration of molybdenum, initially 0.2 mg/L, rose sharply to 45.1 mg/L after 1 h, decreased slightly to an apparent steady-state concentration of ~35 mg/L after 3 h, remained essentially constant through 357 h, then increased sharply to 75.7 mg/L after 500 h, and thereafter declined slowly to 48.9 mg/L after 2014 h. The concentration of barium was negligibly small during most of the experiment. The concentration of strontium, initially 0.28 mg/L, rose sharply to an apparent steady-state concentration of ~0.7 mg/L after 1 h, remained more or less constant through 44 h, and then decreased gradually to a new apparent steady-state concentration for ~0.3 mg/L (the initial concentration) after 1197 h. The concentration of cesium, initially ~3.4 mg/L, increased sharply to 47.6 mg/L after 1 h, remained more or less constant through 20 h, then increased sharply to 109.7 mg/L after 44 h, and thereafter decreased to an apparent steady-state concentration of ~30 mg/L after 357 h. Data for iodine are of suspect validity, and they are being disregarded by BWIP. The concentration of uranium, initially 0 mg/L, increased rapidly to 1.55 mg/L after 1 h and then steadily decreased to a minimum value of ~0.1 mg/L after 2014 h.

B.2.5.3 300°C (run BSF-3)

The concentration of molybdenum, initially 1.3 mg/L, gradually increased to an apparent steady-state concentration of ~55 mg/L after 19 h, remained more or less constant through 1075 h, and then gradually declined to 18.9 mg/L after 2875 h. The concentration of barium, initially 1.5 mg/L, varied erratically between 0 and 1.3 mg/L during the experiment. The concentration of strontium, initially 0.21 mg/L, rose slightly to 0.34 mg/L after 3 h and thereafter slowly decreased to an apparent steady-state concentration of ~0.2 mg/L (the initial concentration) after 571 h. The concentration of cesium, initially 3.4 mg/L, rose sharply to 48.3 mg/L after 1 h, remained constant through 3 h, then decreased erratically to 11.1 mg/L after 571 h, and thereafter gradually rose to 46.8 mg/L after 2875 h. The concentration of iodine, initially 0 mg/L, increased to an apparent steady-state concentration of ~4 mg/L after just 1 h, then increased to 5.6 mg/L after 236 h, and thereafter rose to an apparent inventory-limited concentration of ~11 mg/L after 571 h. Data for uranium are sparse, but after 42 h the concentration of this element appears to have reached a steady-state concentration of ~0.1 mg/L.

B.3 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED CHLW BOROSILICATE GLASS + GROUNDWATER

Experiments on this system were performed by geochemists at Arizona State University and are described by Apted and Myers (1982) and Myers et al. (1983).

B.3.1 Starting Materials

Starting materials were simulated CHLW borosilicate glass (Appendix A, Table A.2) and GR-A synthetic groundwater (Appendix A, Table A.6) in a 1:10 ratio.

B.3.2 Experimental Conditions

Experiments were performed at 30 MPa and 100°C (run GLSW 3-1), 200°C (run GLSW 2-1), and 300°C (run GLSW 1-2) for 2584 h, 3020 h, and 990 h, respectively.

B.3.3 Changes in Groundwater Composition

Measured changes in the compositions of groundwaters at 100, 200, and 300°C are as follows [see Myers et al. (1983, Tables A-10, A-12, and A-14)].

B.3.3.1 100°C (run GLSW 3-1)

The concentration of sodium, initially 250 mg/L, rose steadily during the experiment, reaching a concentration of 2054 mg/L after 2584 h. The concentration of silicon, initially 62 mg/L, rose sharply to 151 mg/L after 6 h and thereafter continued to increase steadily, reaching a maximum of 979 mg/L after 2584 h. The concentration of boron, initially 0 mg/L, increased sharply to ~62 mg/L after 6 h and then continued to rise steadily during the rest of the experiment, reaching a concentration of 544 mg/L after 2584 h.

B.3.3.2 200°C (run GLSW 2-1)

The concentration of sodium, initially 250 mg/L, rose sharply to 1150 mg/L after 3 h, increased steadily to 4450 mg/L after 1533 h, and thereafter dropped to 3770 mg/L after 3020 h. The concentration of silicon, initially 62 mg/L, rose sharply to 640 mg/L after 3 h, then increased steadily to 1330 mg/L after 1533 h, and thereafter decreased to 805 mg/L after 3020 h. The concentration of boron, initially 0 mg/L, increased sharply to 470 mg/L after 3 h, then rose more or less steadily to 2310 mg/L after 912 h, and thereafter declined slightly to 2060 mg/L after 3020 h.

B.3.3.3 300°C (run GLSW 1-2)

The concentration of sodium, initially 250 mg/L, rose sharply to 2600 mg/L after 1 h, then rose to 3800 mg/L after 8.5 h, gradually decreased to 2800 mg/L after 100 h, increased again to 3500 mg/L after 772 h, and thereafter increased sharply to 4510 mg/L after 990 h. The concentration of silicon, initially 62 mg/L, increased sharply to 1060 mg/L after 1 h, then increased steadily to an apparent steady-state concentration of ~1260 mg/L after 15.5 h, and thereafter remained more or less constant. The concentration of boron, initially 0 mg/L, rose sharply to 1610 mg/L after 1 h and thereafter increased erratically to an apparent steady-state concentration of ~3100 mg/L after 28 h.

B.3.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains. Borosilicate glass fragments occur as rounded grains, indicating partial dissolution during experimentation.

The secondary minerals/solid phases that formed at 100, 200, and 300°C are as follows.

100°C (run GLSW 3-1): none detected.

200°C (run GLSW 2-1): sodium-uranium silicate.

300°C (run GLSW 1-2): weeksite, quartz, laplandite, and coffinite.

The Na-U silicate (not coffinite) formed in run GLSW 2-1 was found to contain minor Fe, Zn, and Cl, and a still smaller amount of Cs. This phase is believed to form because there are insufficient amounts of potassium and aluminum present to permit the formation of complex assemblages of secondary minerals. Also, two types of quench phases were detected in the solid experimental products of run GLSW 1-2: (1) a white uranium silicate phase containing minor Na and Al and traces of Nd and Mo; and (2) a finely fibrous to acicular crystalline phase of unknown composition.

B.3.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 100, 200, and 300°C are as follows [see pertinent run tables in Myers et al. (1983, Tables A-10, A-12, and A-14), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1983, Table 8.2) which are summarized in Table B.3].

B.3.5.1 100°C (run GLSW 3-1)

The concentration of molybdenum, initially 0 mg/L, increased sharply to ~61 mg/L after 6 h and then continued to rise during the rest of the experiment, reaching 412 mg/L after 2584 h. The concentration of barium, initially 0 mg/L, increased gradually and more or less steadily to 1.53 mg/L after 836 h, remained constant through 1240 h, and then decreased to 1.08 mg/L after 2584 h. The concentration of strontium, initially 0 mg/L, rose gradually and erratically to 1.06 mg/L after 836 h, remained constant through 1240 h, and then decreased to 0.73 mg/L after 2584 h.

B.3.5.2 200°C (run GLSW 2-1)

The concentration of molybdenum, initially 0 mg/L, increased sharply to 123 mg/L after 3 h and thereafter rose steadily to an apparent steady-state concentration of ~650 mg/L after 912 h. The concentration of barium, initially 0 mg/L, at first apparently increased sharply to 0.45 mg/L after 12 h and thereafter decreased to an apparent (and erratic) steady-state concentration of ~0.05 mg/L after 54 h. The concentration of strontium, initially 0 mg/L, apparently reached a steady-state concentration of ~0.1 mg/L after 12 h.

B.3.5.3 300°C (run GLSW 1-2)

The concentration of molybdenum, initially 0 mg/L, increased sharply to 660 mg/L after 1 h and then rapidly increased erratically to an apparent steady-state concentration of ~1300 mg/L after 52 h. The concentration of barium, initially 0 mg/L, apparently increased sharply (but erratically) to 0.89 mg/L after 15.5 h and thereafter declined sharply to an

apparent steady-state concentration of ~ 0.1 mg/L after 28 h. The concentration of strontium, initially 0 mg/L, increased immediately to an apparent steady-state concentration of ~ 0.02 mg/L and thereafter increased to another apparent steady-state concentration of ~ 0.04 mg/L after 581 h.

B.4 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED CHLW BOROSILICATE GLASS + GROUNDWATER + BASALT

Experiments on this system were performed by geochemists at Arizona State University and are described by Apter and Myers (1982) and Myers et al. (1983).

B.4.1 Starting Materials

Starting materials were simulated CHLW borosilicate glass (Appendix A, Table A.2), Umtanum basalt (Appendix A, Table A.5), and GR-A synthetic groundwater (Appendix A, Table A.6) in a 1:1:20 ratio.

B.4.2 Experimental Conditions

Experiments were performed at 30 MPa and 100°C (run BGLW 3-1), 200°C (run BGLW 2-1), and 300°C (run BGLW 1-1) for 5086 h, 2907 h, and 932 h, respectively.

B.4.3 Changes in Groundwater Composition

Measured changes in the compositions of groundwaters at 100, 200, and 300°C are as follows [see Myers et al. (1983, Tables A-15, A-16, and A-17)].

B.4.3.1 100°C (run BGLW 3-1)

The concentration of sodium, initially 250 mg/L, rose more or less steadily to an apparent steady-state concentration of ~700 mg/L after 792 h. The concentration of silicon, initially 62 mg/L, increased steadily to a maximum concentration of 426 mg/L after 792 h and then slowly decreased to 363 mg/L after 5086 h. The concentration of boron, initially 0 mg/L, rose to 122 mg/L after 792 h and thereafter continued to rise slowly, reaching a concentration of 162 mg/L after 5086 h.

B.4.3.2 200°C (run BGLW 2-1)

The concentration of sodium, initially 250 mg/L, rose more or less steadily during the experiment, reaching a concentration of ~2000 mg/L after 2907 h. The concentration of silicon, initially 62 mg/L, increased fairly steadily to an apparent steady-state concentration of ~1200 mg/L after 1969 h. The concentration of boron, initially 0 mg/L, rose more or less steadily during the experiment, reaching 920 mg/L after 2907 h.

B.4.3.3 300°C (run BGLW 1-1)

The concentration of sodium, initially 250 mg/L, increased very rapidly to 2460 mg/L after 8 h, decreased to 1860 mg/L after 16 h, then rose erratically to 2270 mg/L after 134 h, and thereafter slowly decreased to 2050 mg/L after 932 h. The concentration of silicon, initially 62 mg/L, rose rapidly to 1460 mg/L after 8 h, decreased to 1180 mg/L after 16 h, then increased again to 1340 mg/L after 31 h, and thereafter slowly

decreased to a concentration of 1020 mg/L after 932 h. The concentration of boron, initially 0 mg/L, rose very rapidly to an apparent steady-state concentration of ~1510 mg/L after just 1 h.

B.4.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains. Borosilicate glass fragments occur as rounded grains, and, in 300°C experiments, became coated with secondary solid phases. The rounded nature of the glass grains indicates partial dissolution during experimentation. The primary basalt minerals exhibited little or no evidence of alteration and appeared to be present in original amounts. By contrast, the surfaces of grains of the glass-rich basalt mesostasis were etched and pitted, indicating partial and uneven dissolution. Radionuclide-bearing crystalline phases present in the original glass (e.g., ruthenium oxide, metallic palladium, and a chromium-iron-zinc spinel) remained unaltered during the experiments.

The secondary minerals/solid phases that formed at 100, 200, and 300°C are as follows.

100°C (run BGLW 3-1): none detected.

200°C (run BGLW 2-1): sodium-potassium feldspar.

300°C (run BGLW 1-1): weeksite, quartz, laplandite, boltwoodite, pollucite, and coffinite.

In run BGLW 2-1, silica was found as coatings on the grains of basalt and borosilicate glass, and is believed to be a quench phase. Two types of quench phases were detected in run BGLW 1-1: (1) a white uranium

silicate phase containing minor Na and Al and traces of Nd and Mo; and (2) a finely fibrous to acicular crystalline phase of unknown composition.

B.4.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 100, 200, and 300°C are as follows [see pertinent run tables in Myers et al. (1983, Tables A-15, A-16, and A-17), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1983, Table 8.2) which are summarized in Table B.4].

B.4.5.1 100°C (run BGLW 3-1)

The concentration of molybdenum, initially 0 mg/L rose steadily to ~54 mg/L after 405 h and thereafter continued to increase slowly to a concentration of ~69 mg/L after 5086 h. The concentration of barium, initially 0 mg/L, rose steadily to a maximum concentration of 1.2 mg/L after 792 h and then decreased steadily thereafter to a concentration of 0.47 mg/L after 5086 h. The concentration of strontium, initially 0 mg/L, rose steadily to a maximum concentration of 0.74 mg/L after 405 h and then decreased steadily thereafter to a concentration of 0.28 mg/L after 5086 h.

B.4.5.2 200°C (run BGLW 2-1)

The concentration of molybdenum, initially 0 mg/L, rose more or less steadily throughout the experiment, reaching a concentration of 161 mg/L

after 2907 h. The concentration of barium, initially 0 mg/L, at first increased to 0.22 mg/L after 47 h and then rapidly decreased to an apparent steady-state concentration of ~ 0.06 mg/L after 157 h. The concentration of strontium, initially 0 mg/L, increased to 0.07 mg/L after 2 h and thereafter decreased slowly to an apparent steady-state concentration of ~ 0.02 mg/L after 84 h.

B.4.5.3 300°C (run BGLW 1-1)

The concentration of molybdenum, initially 0 mg/L, rose very rapidly to an apparent (and somewhat erratic) steady-state concentration of ~ 600 mg/L after just 1 h. The concentration of barium, initially 0 mg/L, apparently rose erratically to a maximum concentration of 0.21 mg/L after 134 h and thereafter decreased erratically to 0.06 mg/L after 932 h. The concentration of strontium, initially 0 mg/L, increased to 0.03 mg/L after 1 h and thereafter decreased to an apparent steady-state concentration of ~ 0.01 mg/L after 8 h.

B.5 RESULTS OF EXPERIMENTS ON THE SYSTEM: ^{99}Tc -DOPED SIMULATED CHLW BOROSILICATE GLASS + GROUNDWATER

The single experiment on this system, which was performed by staff members of the Pacific Northwest Laboratory (PNL) and the Westinghouse Hanford Corporation (WHC), is described by Myers et al. (1983) and Coles (1983).

B.5.1 Starting Materials

Starting materials were ^{99}Tc -doped simulated CHLW borosilicate glass (Appendix A, Table A.3) and GR-W synthetic groundwater (Appendix A, Table A.6) in a 1:10 ratio.

B.5.2 Experimental Conditions

Experiments were performed at 30 MPa and 200°C (run B-48-01) for 2632 h.

B.5.3 Changes in Groundwater Composition

Measured changes in the composition of groundwater at 200°C are as follows [see Myers et al. (1983, Table A-19)].

B.5.3.1 200°C (run B-48-01)

The concentration of sodium, initially 410 mg/L, increased somewhat erratically to an apparent steady-state concentration of ~2000 mg/L after 1629 h. The concentration of silicon, initially 35 mg/L, increased somewhat erratically to 970 mg/L after 2296 h and thereafter decreased to 777 mg/L after 2632 h. The concentration of SO_4^{2-} , initially 172 mg/L, increased slightly to an apparent steady-state concentration of ~200 mg/L after 1629 h. The concentration of boron, initially 0 mg/L, increased sharply to 321 mg/L after 19 h, increased gradually to 480 mg/L after 957 h, decreased to 350 mg/L after 1629 h, then rose from 350 mg/L after 1960 h to 530 mg/L after 2296 h, and thereafter decreased to 460 mg/L after 2632 h.

B.5.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains. Borosilicate glass fragments occur as rounded grains, indicating partial dissolution during experimentation.

The secondary minerals/solid phases that formed at 200°C are as follows.

200°C (run B-48-01): sodium-uranium silicate.

B.5.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 200°C are as follows [see pertinent run table in Myers et al. (1983, Table A-19)].

B.5.5.1 200°C (run B-48-01)

The concentration of ^{99}Tc , initially 0 mg/L, increased sharply to 25.2 mg/L after 19 h and then gradually rose to an apparent steady-state concentration of ~50 mg/L after 1293 h. The concentration of molybdenum, initially 0 mg/L, increased sharply to 147 mg/L after 19 h and then gradually increased to an apparent steady-state concentration of ~275 mg/L after 1960 h.

B.6 RESULTS OF EXPERIMENTS ON THE SYSTEM: ^{99}Tc -DOPED SIMULATED CHLW BOROSILICATE GLASS + GROUNDWATER + BASALT

The single experiment on this system, which was performed by staff members of the PNL and WHC, is described by Myers et al. (1983) and Coles (1983b).

B.6.1 Starting Materials

Starting materials were ^{99}Tc -doped simulated CHLW borosilicate glass (Appendix A, Table A.3), Umtanum basalt (Appendix A, Table A.5), and GR-W synthetic groundwater (Appendix A, Table A.6) in a 1:1:20 ratio.

B.6.2 Experimental Conditions

Experiments were performed at 30 MPa and 200°C (run B-48-02) for 2654 h.

B.6.3 Changes in Groundwater Composition

Measured changes in the composition of groundwater at 200°C are as follows [see Myers et al. (1983, Table A-20)].

B.6.3.1 200°C (run B-48-02)

The concentration of sodium, initially 410 mg/L, increased more or less steadily to an apparent (and erratic) steady-state concentration of ~650 mg/L after 975 h. The concentration of silicon, initially 35 mg/L, increased rapidly to 176 mg/L after 22 h and thereafter continued to increase to an apparent (and erratic) steady-state concentration of ~600 mg/L after 1311 h. The concentration of SO_4^{2-} , initially 172 mg/L, increased slightly to an apparent (and erratic) steady-state concentration of ~190 mg/L after 22 h. The concentration of boron, initially 0 mg/L, increased erratically during the experiment, reaching a concentration of 45 mg/L after 2654 h.

B.6.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains. Borosilicate glass fragments occur as rounded grains, indicating partial dissolution during experimentation. The primary basalt minerals exhibited little or no evidence of alteration and appeared to be present in original amounts. By contrast, the surfaces of grains of the glass-rich basalt mesostasis were etched and pitted, indicating partial and uneven dissolution.

The secondary minerals/solid phases that formed at 200°C are as follows.
200°C (run B-48-02): sodium-potassium feldspar.

B.6.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 200°C are as follows [see pertinent run table in Myers et al. (1983, Table A-20)].

B.6.5.1 200°C (run B-48-02)

The concentration of ^{99}Tc , initially 0 mg/L, increased to an apparent steady-state concentration of ~2.5 mg/L after 22 h, remained essentially constant through 644 h, and thereafter declined to a negligibly small concentration (<0.01 mg/L) after 1311 h. The concentration of molybdenum, initially 0 mg/L, increased erratically to a concentration of 9.34 mg/L after 2151 h and thereafter increased abruptly to 30 mg/L after 2654 h.

B.7 RESULTS OF EXPERIMENTS ON THE SYSTEM: ^{237}Np - AND ^{239}Pu -DOPED SIMULATED CHLW BOROSILICATE GLASS + GROUNDWATER

The single experiment on this system was performed by staff members of the PNL and WHC and is described by Coles (1983b).

B.7.1 Starting Materials

Starting materials were ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass (Appendix A, Table A.3) and GR-W synthetic groundwater (Appendix A, Table A.6) in a 1:10 ratio.

B.7.2 Experimental Conditions

Experiments were performed at 30 MPa and 200°C (run B-48-03) for 2304 h.

B.7.3 Changes in Groundwater Composition

Measured changes in the composition of groundwater at 200°C are as follows [see Coles (1983b, Table A-3)].

B.7.3.1 200°C (run B-48-03)

(The following results were obtained from diluted solutions that were passed through a 4000 Å filter.) The concentration of sodium, initially 410 mg/L, increased sharply to 1060 mg/L after 16 h, rose to 1600 mg/L after 100 h, then decreased sharply to 640 mg/L after 264 h, and thereafter increased somewhat erratically to an apparent steady-state concentration of ~1900 mg/L after 2304 h. The concentration of silicon, initially 35 mg/L, increased sharply to 490 mg/L after 16 h, rose to ~680 mg/L after 100 h, then declined to 380 mg/L after 264 h, and thereafter increased fairly steadily to an apparent steady-state concentration of ~850 mg/L. The concentration of SO_4^{2-} , initially 172 mg/L, increased slightly to an apparent steady-state concentration of ~200 mg/L after 100 h. The concentration of boron, initially 0 mg/L, increased sharply to 378 mg/L after 100 h, then decreased to 180 mg/L after 264 h, and thereafter increased to an apparent steady-state concentration of ~550 mg/L after 840 h.

B.7.4 Solid Experimental Products

Data on solid experimental products are to be presented in a future BWIP report.

B.7.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 200°C are as follows [see pertinent run table in Coles (1983b, Table A-3)].

B.7.5.1 200°C (run B-48-03)

Results for ^{237}Np and ^{239}Pu , presented below, were obtained from undiluted and unfiltered solutions, whereas results for molybdenum were obtained from diluted solutions that were passed through a 4000 Å filter.

The concentration of ^{237}Np , initially 0 mg/L, increased sharply to 0.04 mg/L after 16 h and then decreased sharply to an apparent steady-state concentration of ~0.0025 mg/L after 840 h. The concentration of ^{239}Pu , initially 0 mg/L, increased sharply to ~0.0006 mg/L after 16 h, then decreased sharply to 0.0002 mg/L after 100 h, and thereafter decreased slowly to an apparent steady-state concentration of ~0.0001 mg/L after 840 h. The concentration of molybdenum, initially 0 mg/L, increased sharply to 104 mg/L after 16 h and then gradually increased to an apparent steady-state concentration of ~310 mg/L sometime before 2302 h (data for 264-1824 h are missing).

B.8 RESULTS OF EXPERIMENTS ON THE SYSTEM: ^{237}Np - and ^{239}Pu -DOPED SIMULATED CHLW BOROSILICATE GLASS + GROUNDWATER + BASALT

The single experiment on this system was performed by staff members of the PNL and WHC and is described by Coles (1983b).

B.8.1 Starting Materials

Starting materials were ^{237}Np - and ^{239}Pu -doped simulated CHLW borosilicate glass (Appendix A, Table A.3), Umtanum basalt (Appendix A, Table A.5), and GR-W synthetic groundwater (Appendix A, Table A.6) in a 1:1:20 ratio.

B.8.2 Experimental Conditions

Experiments were performed at 30 MPa and 200°C (run B-48-04) for 2175 h.

B.8.3 Changes in Groundwater Composition

Measured changes in the composition of groundwater at 200°C are as follows [see Coles (1983b, Table A-4)].

B.8.3.1 200°C (run B-48-04)

(The following results were obtained from diluted solutions that were passed through a 4000 Å filter.) The concentration of sodium initially 410 mg/L, increased slowly and erratically to a maximum value of 718 mg/L after 2173 h. The concentration of silicon, initially 35 mg/L, increased rapidly to 320 mg/L after 160 h, then increased to 394 mg/L after 832 h, and thereafter rose to an apparent steady-state concentration of ~625 mg/L after 1167 h. The concentration of SO_4^{2-} , initially 172 mg/L, increased slightly to an apparent (and erratic) steady-state concentration of ~200 mg/L sometime before 496 h (data for 160 h are missing). The concentration of boron, initially 0 mg/L, increased sharply to 52 mg/L after 832 h, then decreased sharply to ~5 mg/L after 1503 h, and thereafter increased again to 33 mg/L after 2173 h.

B.8.4 Solid Experimental Products

Data on solid experimental products are to be presented in a future BWIP report.

B.8.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 200°C are as follows [see pertinent run table in Coles (1983b, Table A-4)].

B.8.5.1 200°C (run B-48-04)

(Results for ^{237}Np and ^{239}Pu presented below were obtained from undiluted and unfiltered solutions, whereas results for molybdenum were obtained from diluted solutions that were passed through a 4000 Å filter.) The concentration of ^{237}Np , initially 0 mg/L, increased sharply to 0.012 mg/L after 160 h, decreased slightly to 0.008 mg/L after 496 h, then rose fairly steadily to 0.070 mg/L after 1503 h, and thereafter declined rather sharply to an apparent steady-state concentration of ~0.031 mg/L after 1839 h. The concentration of ^{239}Pu , initially 0 mg/L, increased sharply to ~0.001 mg/L after 16 h, then increased fairly steadily to a maximum value of 0.0072 mg/L after 1167 h, and thereafter decreased slowly and steadily to ~0.0034 mg/L after 2173 h. The concentration of molybdenum, initially 0 mg/L, increased to an apparent steady-state concentration of ~9.0 mg/L sometime before 1503 h (data for 160-1167 h are missing).

B.9 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED DHLW BOROSILICATE GLASS + GROUNDWATER + BASALT

Experiments on this system were performed by BWIP staff members and are described by Myers et al. (1983).

B.9.1 Starting Materials

Starting materials were simulated DHLW borosilicate glass (Appendix A, Table A.4), Umtanum basalt (Appendix A, Table A.5), and GR-3 synthetic groundwater (Appendix A, Table A.6) in a 1:1:20 ratio.

B.9.2 Experimental Conditions

Experiments were performed at 10 MPa, 90°C (run D7-1) and 150°C (run D8-1) for 2228 h and 2202 h, respectively.

B.9.3 Changes in Groundwater Composition

Measured changes in the compositions of groundwaters at 90 and 150°C are as follows [see Myers et al. (1983, Tables A-21 and A-23)].

B.9.3.1 90°C (run D7-1)

The concentration of sodium, initially 358 mg/L, increased sharply to ~1306 mg/L after 812 h and thereafter increased only slightly to ~1382 mg/L after 2228 h. The concentration of silicon, initially 35.6 mg/L, increased sharply to an apparent steady-state concentration of ~630 mg/L after 331 h. The concentration of boron, initially 0 mg/L, increased sharply to ~221 mg/L after 331 h and thereafter slowly increased to a concentration of ~368 mg/L after 2228 h.

B.9.3.2 150°C (run D8-1)

The concentration of sodium, initially 358 mg/L, increased continuously during the experiment, reaching ~2168 mg/L after 2202 h. The concentration of silicon, initially 35.6 mg/L, increased sharply to 401 mg/L after 144 h and thereafter increased more or less steadily to a concentration of ~1093 mg/L after 2202 h. The concentration of boron, initially 0 mg/L, increased more or less steadily during the experiment, reaching a maximum concentration of ~681 mg/L after 2202 h.

B.9.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains. Borosilicate glass fragments occur as rounded grains, indicating partial dissolution during experimentation. The primary basalt minerals exhibited little or no evidence of alteration and appeared to be present in original amounts. By contrast, the surfaces of grains of the glass-rich basalt mesostasis were etched and pitted, indicating partial and uneven dissolution.

The secondary minerals/solid phases that formed at 90 and 150°C are as follows.

90°C (run D7-1): none detected.

150°C (run D8-1): none detected.

B.9.5 Concentrations of Radionuclides and/or Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclides and/or radionuclide-analog elements in groundwaters at 90 and 150°C are as

follows [see pertinent run tables in Myers et al. (1983, Tables A-21 and A-23), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1983, Table 8.2) which are summarized in Table B.5].

B.9.5.1 90°C (run D7-1)

The concentration of strontium, initially 0 mg/L, reached an apparent steady-state concentration of ~0.005 mg/L after 331 h.

B.9.5.2 150°C (run D8-1)

The concentration of strontium, initially 0 mg/L, reached an apparent steady-state concentration of ~0.003 mg/L after 144 h, but after 888 h it began to increase, reaching 0.018 mg/L after 2202 h.

Table B.1. Steady-state concentrations (mg/L) of radionuclide-analog elements in the system: simulated spent fuel + groundwater

Element	SF + W		
	100°C	200°C	300°C
Ba	0.18	0.12	0.03
Cs	0.05 ^a	NA	NA
I	NA	NA	NA
Mo	71	68	150
Ni	NI	NI	NI
Pb	0.23 ^a	NA	0.35
Pd	0.036 ^a	NA	NA
Rb	NI	NI	NI
Re	NA	NA	NA
Sm	NA	NA	NA
Sr	0.04	0.01	0.007
Tc	NI	NI	NI
Te	0.19	0.13	0.10
Th	NA	NA	NA
U	NA	NA	NA
Zr	0.02	0.12 ^a	0.02

SF = Simulated spent fuel (Appendix A, Table A.1).

W = GR-3 synthetic groundwater (Appendix A, Table A.6).

NA = Not analyzed.

NI = Not in inventory.

^aNon-steady-state.

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 8.2, September 1983.

Table B.2. Steady-state concentrations (mg/L) of radionuclide-analog elements in the system: simulated spent fuel + groundwater + basalt

Element	SF + B + W		
	100°C	200°C	300°C
Ba	1.0	<0.03	<0.03
Cs	50.0	30.5	46.8
I	11.0 ^a	0.4 ^b	11.2 ^a
Mo	75	76	18.9
Ni	NI	NI	NI
Pb	NA	NA	NA
Pd	<0.1	0.1	<0.1
Rb	NI	NI	NI
Re	NA	<0.02	1.8 ^b
Sm	NA	NA	0.03
Sr	2.1	0.36	0.21
Tc	NI	NI	NI
Te	<0.1	0.1	<0.1
Th	<0.2	0.2	<0.2
U	0.29	0.10	0.13
Zr	NA	NA	NA

SF = Simulated spent fuel (Appendix A, Table A.1).

B = Umtanum basalt (Appendix A, Table A.5).

W = GR-3 synthetic groundwater (Appendix A, Table A.6).

NA = Not analyzed.

NI = Not in inventory.

^aInventory limited.

^bNon-steady-state.

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 8.2, September 1983.

Table B.3. Steady-state concentrations (mg/L) of radionuclide-analog elements in the system: simulated CHLW borosilicate glass + groundwater

Element	CHLW + W		
	100°C	200°C	300°C
Ba	1.27	0.03	0.18
Cs	NA	20.2	NA
I	NI	NI	NI
Mo	188	650	1290 ^a
Ni	NA	NA	NA
Pb	NI	NI	NI
Pd	NA	<0.008	NA
Rb	NA	NA	60
Re	NI	NI	NI
Sm	NA	0.05	NA
Sr	0.89	0.004	0.04
Tc	NI	52.5	NI
Te	NA	NA	NA
Th	NA	NA	NA
U	NA	NA	NA
Zr	NA	NA	NA

CHLW = Simulated CHLW borosilicate glass (Appendix A, Table A.2).

W = GR-A synthetic groundwater (Appendix A, Table A.6).

NA = Not analyzed.

NI = Not in inventory.

^aInventory limited.

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 8.2, September 1983.

Table B.4. Steady-state concentrations (mg/L) of radionuclide-analog elements in the system: simulated CHLW borosilicate glass + groundwater + basalt

Element	CHLW + B + W		
	100°C	200°C	300°C
Ba	0.47	0.07	0.06
Cs	2.2	16.1	NA
I	NI	NI	NI
Mo	69	161	620 ^a
Ni	NA	NA	NA
Pb	NI	NI	NI
Pd	<0.26	<1.27	NA
Rb	NA	6.5	10
Re	NI	NI	NI
Sm	0.18	0.29	NA
Sr	0.28	0.02	0.02
Tc	NI	0.0015	NI
Te	NA	NA	NA
Th	NA	NA	NA
U	NA	NA	NA
Zr	NA	NA	NA

CHLW = Simulated CHLW borosilicate glass (Appendix A, Table A.2).

B = Umtanum basalt (Appendix A, Table A.5).

W = GR-A synthetic groundwater (Appendix A, Table A.6).

NA = Not analyzed.

NI = Not in inventory.

^aInventory limited.

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 8.2, September 1983.

Table B.5. Steady-state concentrations (mg/L) of radionuclide-analog elements in the system: simulated DHLW borosilicate glass + groundwater + basalt

Element	DHLW + B + W	
	90°C	150°C
Ba	0.037	0.012
Cs	NA	NA
I	NI	NI
Mo	NI	NI
Ni	<0.026	<0.026
Pb	<0.155	<0.155
Pd	NI	NI
Rb	NI	NI
Re	NI	NI
Sm	NI	NI
Sr	0.006	0.018
Tc	NI	NI
Te	NI	NI
Th	NI	NI
U	NI	NI
Zr	<0.014	<0.014

DHLW = Simulated DHLW borosilicate glass (Appendix A, Table A.4).

B = Umtanum basalt (Appendix A, Table A.5).

W = GR-3 synthetic groundwater (Appendix A, Table A.6).

NA = Not analyzed.

NI = Not in inventory.

Source: MYERS 1983. J. Myers, M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials under Conditions Expected in a Nuclear Waste Repository in Basalt, SD-BWI-TI-141, Rev. 0-0, Table 8.2, September 1983.