OAK RIDGE NATIONAL LABORATORY
OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.

POST OFFICE BOX X
OAK RIDGE, TENNESSEE 37831

WM DOCKET CONTROL CENTER

'86 NOV 10 P12:11

Nov. 7, 1986

WM-RES
WM Record File B0287 B0290 ORNL
Distribution: D Brooks
(Return to WM, 623-SS)

WM Project 10, 11, 16
Docket No.
PDR ✓
LPDR B,N,S

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

Dear Dave:

At your request I am enclosing the following: (1) a copy of the final version of the topical report on solubility information for the Hanford Site and (2) information on the quality assurance programs at ORNL that affect the two NRC projects B0287 and B0290. The topical report is now being edited and will be ready for final printing within a couple of weeks. If you have questions concerning either enclosure, please call me.

Sincerely,

Gary K Jacobs

Gary K. Jacobs
Manager, NRC Waste Programs
Environmental Sciences Division
Building 1505, MS-038, FTS/626-0567

GKJ/

Enclosures: (1) topical report, (2) QA information
SEE FILE JACKET

cc w/o enclosures:

Office of the Director, NMSS (Attn: Program Support Branch)
Division Director, NMSS Division of Waste Management (2)
Branch Chief, Waste Management Branch, RES
P. S. Justus, Chief, Geotechnical Branch, NMSS
K. C. Jackson, Geotechnical Branch, NMSS
A. P. Malinauskas
GKJ File

8611200387 861107
PDR WMRES EXIORNL
B-0287 PDR

3495

Received w/Ltr Dated 11/7/86
8611200387

NUREG/CR-4024
ORNL/TM-9415
Dist. Category RW

REVIEW AND ASSESSMENT OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES/ CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS IN THE SYSTEMS: SIMULATED WASTE FORM ± UMTANUM BASALT + GRANDE RONDE GROUNDWATER

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

Prepared by the
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

ABSTRACT

This document reviews selected information on the measured aqueous concentrations and calculated "true aqueous solubilities" of radionuclide-analog elements in various simulated waste form ± Umtanum basalt + Grande Ronde groundwater systems. Most of the available information on these systems has been generated as a result of the ongoing Department of Energy (DOE) effort to assess the feasibility of constructing and operating a nuclear waste repository in basalt (NWRB) at Hanford, Washington. Therefore, the commentary in this document focuses on information provided in key reports and articles published by DOE-Hanford staff members and contractors.

DOE-Hanford information on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems can be divided into two major categories: (1) experimental data for "high" temperatures (90 to 300°C), and (2) calculational data for "low" temperatures (25 to 90°C). Accordingly, the assessments of DOE-Hanford information on the solubilities/concentrations of radionuclide-analog elements offered in this report have been divided into three major sections: (1) a section containing detailed discussions of experimental data on the solubilities/concentrations of radionuclide-analog elements in various simulated waste form ± Umtanum basalt + Grande Ronde groundwater systems at 10 to 30 MPa, 90 to 300°C; (2) a section containing detailed discussions of calculated solubilities for radionuclide-analog elements in basalt-groundwater systems at 1 atm, 25 to 60°C; and (3) a summary of DOE-Hanford information on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems relevant to an NWRB.

Finally, this document deals exclusively with information on the solubilities/concentrations of radionuclide-analog elements available prior to March, 1984 (the date of publication of the report by Myers et al., 1984a). Therefore, this document contains no discussions of the solubilities/concentrations of radionuclides, nor is there any attempt to treat the small amount of information on the solubilities/concentrations of radionuclide-analog elements that has been obtained recently from DOE-Hanford hydrothermal experiments with "tracer-doped" and "fully-loaded" waste forms.

TABLE OF CONTENTS

Page

ABSTRACT iii
1. EXECUTIVE SUMMARY 1-1
1.1 DOE-HANFORD EXPERIMENTAL DATA ON THE SOLUBILITIES/ CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS IN THE SYSTEMS SIMULATED WASTE FORM ± UMTANUM BASALT + GRANDE RONDE GROUNDWATER AT 10 TO 30 MPa, 90 TO 300°C 1-1
1.2 CALCULATED SOLUBILITIES OF RADIONUCLIDE-ANALOG ELEMENTS IN BASALT-GROUNDWATER SYSTEMS AT 1 ATM, 25 TO 60°C . . . 1-3
2. INTRODUCTION 2-1
2.1 REGULATORY CONTEXT OF RADIONUCLIDE "SOLUBILITY" INFORMATION 2-1
2.2 GEOCHEMICAL CONTEXT OF RADIONUCLIDE "SOLUBILITY" INFORMATION 2-3
2.3 PURPOSE AND SCOPE OF THIS REPORT 2-4
2.4 BRIEF DESCRIPTION OF THE HANFORD SITE 2-5
3. DOE-HANFORD INFORMATION ON THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS AT 10 TO 30 MPa, 90 TO 300°C 3-1
3.1 DOE-HANFORD APPROACH TO DATA DEVELOPMENT 3-1
3.1.1 DOE-Hanford-Cited Premises Concerning Post-closure Events, Geochemical Conditions, and Barrier-Materials/Groundwater Interactions in an NWRB at the Hanford Site 3-1
3.1.2 DOE-Hanford-Cited Premises Concerning Procedures for Hydrothermal Experiments on Barrier Materials + Groundwater Systems 3-4
3.2 REVIEW OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES/ CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS 3-9
3.2.1 Experimental Results 3-9
3.2.1.1 Key DOE-Hanford Information on the Solubilities of Radionuclide-Analog Elements at 90 to 300°C 3-9
3.2.1.1.1 Molybdenum 3-9
3.2.1.1.2 Barium 3-11
3.2.1.1.3 Strontium 3-12
3.2.1.1.4 Cesium 3-14
3.2.1.1.5 Iodine 3-14
3.2.1.1.6 Uranium 3-15
3.2.1.2 Additional Significant Experimental Information 3-15
3.2.2 Calculation Results 3-19
3.3 DOE-HANFORD-CITED LIMITATIONS OF DOE-HANFORD "SOLUBILITY" INFORMATION 3-20
3.4 ASSESSMENT OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS 3-21

Page

4. DOE-HANFORD INFORMATION ON THE SOLUBILITIES OF RADIONUCLIDE-ANALOG ELEMENTS AT 1 ATM, 25 TO 90°C 4-1
4.1 DOE-HANFORD APPROACH TO DATA DEVELOPMENT 4-1
4.2 REVIEW OF PUBLISHED DOE-HANFORD SOLUBILITY INFORMATION. 4-5
4.2.1 Experimental Results 4-5
4.2.2 Calculational Results 4-5
4.3 DOE-HANFORD-CITED LIMITATIONS OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES OF RADIONUCLIDE-ANALOG ELEMENTS . . . 4-8
4.4 ASSESSMENT OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES OF RADIONUCLIDE-ANALOG ELEMENTS 4-11
5. A SUMMARY OF DOE-HANFORD DATA ON THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS IN BARRIER MATERIALS + GROUNDWATER SYSTEMS 5-1
5.1 THE RATIONALE FOR SEGREGATING THE SOLUBILITY/CONCENTRATION DATA BY SYSTEM AND TEMPERATURE 5-1
5.1.1 Potential Difficulties in Continuing to Classify Solubility/Concentration Data by System and Temperature 5-7
5.2 ADDITIONAL COMPLEXITIES IN EXPERIMENTAL MEASUREMENTS OF THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS. 5-9
5.3 DIFFERENCES BETWEEN THE SOLUBILITIES/CONCENTRATIONS LISTED BY MYERS ET AL. (1984a) AND CORRESPONDING VALUES DEVELOPED BY THE AUTHOR 5-14
5.4 CALCULATED SOLUBILITIES FOR RADIONUCLIDE-ANALOG ELEMENTS AT 25°C 5-14
6. MAJOR CONCLUSIONS 6-1
7. REFERENCES 7-1
APPENDICES
Appendix A: CHEMICAL COMPOSITIONS OF SOLID AND FLUID STARTING MATERIALS FOR "HIGH-TEMPERATURE" (90 TO 300°C) HYDROTHERMAL EXPERIMENTS ON THE SYSTEMS: SIMULATED WASTE FORM ± UMTANUM BASALT + GRANDE RONDE GROUNDWATER. A1
Appendix B: SUMMARIES AND INTERPRETATIONS OF RESULTS OBTAINED FROM EXPERIMENTS PERFORMED ON THE SYSTEMS SIMULATED WASTE FORM ± UMTANUM BASALT + GRANDE RONDE GROUNDWATER AT 10 TO 30 MPa, 90 TO 300°C B1
B.1 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED SPENT FUEL + GR-3 GROUNDWATER . . B2
B.1.1 Starting Materials B2
B.1.2 Experimental Conditions. B2
B.1.3 Changes in the Concentrations of Aqueous Sodium, Silicon, and Sulfate. B3
B.1.3.1 100°C (run D6-8). B3
B.1.3.2 200°C (run D6-1). B3
B.1.3.3 300°C (run D5-1). B4
B.1.4 Solid Experimental Products. B4
B.1.5 Concentrations of Radionuclide-Analog Elements. B4

B.1.5.1 100°C (run D6-8) B5
B.1.5.2 200°C (run D6-1) B5
B.1.5.3 300°C (run D5-1) B5
B.2 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED SPENT FUEL + UMTANUM BASALT + GR-3 GROUNDWATER. B6
B.2.1 Starting Materials B6
B.2.2 Experimental Conditions. B6
B.2.3 Changes in the Concentrations of Aqueous Sodium, Silicon, and Sulfate. B7
B.2.3.1 100°C (run BSF-4) B7
B.2.3.2 200°C (run BSF-2) B7
B.2.3.3 300°C (run BSF-3) B8
B.2.4 Solid Experimental Products. . . . B8
B.2.5 Concentrations of Radionuclide-Analog Elements. B9
B.2.5.1 100°C (run BSF-4) B9
B.2.5.2 200°C (run BSF-2) B10
B.2.5.3 300°C (run BSF-3) B11
B.3 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED CHLW BOROSILICATE GLASS + GR-A GROUNDWATER. B11
B.3.1 Starting Materials B12
B.3.2 Experimental Conditions. B12
B.3.3 Changes in the Concentrations of Aqueous Sodium, Silicon, and Boron. B12
B.3.3.1 100°C (run GLSW 3-1). . . B12
B.3.3.2 200°C (run GLSW 2-1). . . B13
B.3.3.3 300°C (run GLSW 1-2). . . B13
B.3.4 Solid Experimental Products. . . . B13
B.3.5 Concentrations of Radionuclide-Analog Elements. B14
B.3.5.1 100°C (run GLSW 3-1). . . B14
B.3.5.2 200°C (run GLSW 2-1). . . B15
B.3.5.3 300°C (run GLSW 1-2). . . B15
B.4 RESULTS OF EXPERIMENTS ON THE SYSYTEM: SIMULATED CHLW BOROSILICATE GLASS + UMTANUM BALSAT + GR-A GROUNDWATER B16
B.4.1 Starting Materials B16
B.4.2 Experimental Conditions. B16
B.4.3 Changes in the Concentrations of of Aqueous Sodium, Silicon, and Boron. B16
B.4.3.1 100°C (run BGLW 3-1). . . B17
B.4.3.2 200°C (run BGLW 2-1). . . B17
B.4.3.3 300°C (run BGLW 1-1). . . B17
B.4.4 Solid Experimental Products. . . . B18
B.4.5 Concentrations of Radionuclide-Analog Elements. B19
B.4.5.1 100°C (run BGLW 3-1). . . B19
B.4.5.2 200°C (run BGLW 2-1). . . B19
B.4.5.3 300°C (run BGLW 1-1). . . B20

Page

B.5 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED DHLW BOROSILICATE GLASS + UMTANUM BASALT + GR-3 GROUNDWATER B20
B.5.1 Starting Materials B20
B.5.2 Experimental Conditions. B21
B.5.3 Changes in Concentrations of Aqueous Sodium, Silicon, and Boron B21
B.5.3.1 90° (run D7-1). B21
B.5.3.2 150°C (run D8-1). B21
B.5.4 Solid Experimental Products. . . . B22
B.5.5 Concentrations of Radionuclide-Analog Elements. B22
B.5.5.1 90°C (run D7-1) B22
B.5.5.2 150°C (run D8-1). B23

Review and Assessment of DOE-Hanford Information on the Solubilities/ Concentrations of Radionuclide-Analog Elements in the Systems: Simulated Waste Form ± Umtanum Basalt + Grande Ronde Groundwater

J. G. Blencoe

1. EXECUTIVE SUMMARY

DOE-Hanford currently possesses two distinctly different types of information on the solubilities of radionuclide-analog elements in barrier materials + groundwater systems: (1) data on the solubilities/ concentrations of radionuclide-analog elements in the systems simulated waste form ± Umtanum basalt + Grande Ronde groundwater at 10 to 30 MPa, 90 to 300°C; and (2) calculated solubilities for radionuclide-analog elements in basalt-groundwater systems at 1 atm, 25 to 60°C.

1.1 DOE-HANFORD EXPERIMENTAL DATA ON THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS IN THE SYSTEMS SIMULATED WASTE FORM ± UMTANUM BASALT + GRANDE RONDE GROUNDWATER AT 10 TO 30 MPa, 90 TO 300°C

DOE-Hanford experimental data on the solubilities/concentrations of radionuclide-analog elements in the systems simulated waste form ± Umtanum basalt + Grande Ronde groundwater at 10 to 30 MPa, 90 to 300°C, have been described by Apted and Myers (1982), Myers et al. (1984a), and Grandstaff et al. (1984). The systems investigated to date are: simulated spent fuel ± Umtanum basalt + GR-3 groundwater, simulated commercial high-level waste (CHLW) borosilicate glass ± Umtanum basalt + GR-A groundwater, and simulated defense high-level waste (DHLW) borosilicate glass + Umtanum basalt + GR-3 groundwater. Experiments on these systems have yielded a modest amount of data on the solubilities/ concentrations of the radionuclide-analog elements Mo, Ba, Sr, Cs, I,

and U. In many of these experiments, some, but not all, radionuclide-analog elements achieved steady-state concentrations prior to cessation of experimentation.

Experimental data on the systems simulated spent fuel + Umtanum basalt + GR-3 groundwater and simulated CHLW borosilicate glass + Umtanum basalt + GR-A groundwater indicate that, at a given temperature, the final relative solubilities/concentrations of radionuclide-analog elements (mg/L) are typically Mo > Cs > I > Ba ≈ Sr > U. Also, 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.

Additional important observations concerning DOE-Hanford information on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems are as follows:

1. DOE-Hanford experimental data on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems at 90 to 300°C have been obtained under experimental conditions that do not adequately simulate the geochemical conditions which are expected to prevail near the waste packages in a nuclear waste repository in basalt (NWRB) after the containment period. Improved simulation of these geochemical conditions would be effected by conducting barrier materials + groundwater experiments with hydrothermally altered basalt + bentonite mixtures and pieces (not powders) of simulated canister and cladding material.

2. Data on simulated waste form ± basalt + groundwater systems obtained to date do not rule out the possibility that the solubilities/concentrations of some radionuclide-analog elements may be altered significantly by relatively small changes in the composition of the simulated waste form.

3. DOE-Hanford experimental investigations of the solubilities of radionuclide-analog elements in barrier materials + groundwater systems have emphasized acquisition of data from experiments conducted at 10-30 MPa, 90 to 300°C. Consequently, there is a dearth of "solubility" data for radionuclide-analog elements in barrier materials + groundwater systems at 1 atm, 25 to 90°C.

1.2 CALCULATED SOLUBILITIES OF RADIONUCLIDE-ANALOG ELEMENTS IN BASALT-GROUNDWATER SYSTEMS AT 1 ATM, 25 TO 60°C

Most of the DOE-Hanford information on the solubilities of radionuclide-analog elements in basalt-groundwater systems at 1 atm, 25 to 60°C (Early et al., 1982; Early et al., 1984) has been obtained from calculations performed with geochemical computer codes. These calculations are based principally on thermodynamic data for: (1) neutral and ionic aqueous species that are found (or have the potential to exist) in natural groundwaters, (2) aqueous radionuclide-analog-element species and radionuclide-analog-element-bearing crystalline phases, and (3) major and minor rock-forming minerals. Results of these calculations and theoretical considerations indicate that the solubilities of radionuclide-analog elements are sensitive to: (1) groundwater composition, (2) Eh

and pH, (3) the types and thermodynamic stabilities of radionuclide-analog-element-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 radionuclide-analog elements 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 performed by Early et al. also indicate that the solubilities of Se, Pd, Sn, U, and Np exhibit the greatest sensitivity to Eh. Finally, for synthetic Grande Ronde groundwater GR-3 at 25°C and Eh = -0.3 V, calculations performed by Early et al. indicate that the relative solubilities (mol/L) of radionuclide-analog elements 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 radionuclide-analog elements in basalt-groundwater systems at 1 atm, 25 to 90°C, indicates that this approach has the following drawbacks: (1) the data bases for existing geochemical computer codes are incomplete and often contain thermodynamic data which are of dubious accuracy; (2) existing geochemical computer codes cannot fully account for the geochemical effects of radionuclide sorption, precipitation of radionuclide solid solutions, and/or sluggish reaction

kinetics; (3) thermodynamic calculations of the solubilities of radionuclides and radionuclide-analog elements 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°C; and (4) the types and compositions of radionuclide-bearing solids that will actually form in the disturbed zone and far field of an NWRB are not well known at the present time. In view of these difficulties it is concluded that, by themselves, the results of thermodynamic calculations are insufficient to establish the true nature and significance of radionuclide speciation and solubility in basalt-groundwater systems.

2. INTRODUCTION

2.1 REGULATORY CONTEXT OF RADIONUCLIDE "SOLUBILITY" 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 10CRF60.113 (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 EPA regulation 40CFR191 (EPA, 1985), it is stipulated that the repository system must restrict radionuclide releases in accordance with EPA standards which specify permissible <u>cumulative</u> 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, it is widely acknowledged that the technical information and conceptual models used in the performance assessments should be supported by data bases that adequately document the contribution of individual processes and conditions which significantly 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 determined partly by the solubilities/concentrations 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

---

*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 element 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 adsorption or ion exchange, or when the amount of dissolved-plus-suspended element is equal to the entire amount of that element that is present in a barrier material(s) + groundwater system. (In the latter case, the concentration of the nuclide is said to be "inventory limited.")

DOE-Hanford technical activities presently include a vigorous data development program on the solubilities/concentrations of radionuclides under both disturbed-zone ("high" temperature) and repository-ambient ("low" temperature) geochemical conditions.

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 have a significant impact on radionuclide-release rates. 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 be borne in mind that the technical criteria of regulation 10CFR60.113 and the 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 can be anticipated that waste package and site-performance assessments will identify radionuclide solubility/concentration 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 DOE-Hanford information on the solubilities/concentrations of radionuclide-analog elements in various barrier material(s) (waste form, basalt, etc.) + groundwater systems. Investigations of the solubilities/concentrations of radionuclide-analog elements by DOE-Hanford staff members and contractors are one aspect of the multifaceted DOE-Hanford 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. DOE-Hanford contends that the geochemical environments in a nuclear waste repository in basalt (NWRB) at the Hanford Site will be oxygen-deficient (reducing) (DOE, 1986), and under such conditions the solubilities/concentrations of many radionuclides (in particular,

actinide elements) are very low. Thus, it is likely that DOE-Hanford will attempt to take credit for this potentially favorable geochemical condition in their attempts to demonstrate compliance with NRC and EPA regulations concerning containment and release of radionuclides from an NWRB. Should this happen, it will be important for the NRC to be in a position to assess the accuracy, completeness, and relevance of the information possessed by DOE-Hanford concerning the solubilities/ concentrations 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.

DOE-Hanford geologic studies of the Hanford Site (e.g., Myers et al., 1979; Myers and Price, 1981) have provided sufficient geologic information to locate several areas on the site where conditions appear to be suitable for constructing an HLW repository. Furthermore, one of these areas — a 47-km^2 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.

DOE-Hanford 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 Cohassett basalt is the leading candidate repository horizon (Long and WCC, 1984). 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. DOE-HANFORD INFORMATION ON THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS AT 10 TO 30 MPa, 90 TO 300°C

3.1 DOE-HANFORD APPROACH TO DATA DEVELOPMENT

A review of pertinent DOE-Hanford publications (e.g., Apted, 1982; Apted and Myers, 1982; Wood et al., 1983; Myers et al., 1984a) indicates that the DOE-Hanford program for hydrothermal testing of barrier materials 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 DOE-Hanford-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 DOE-Hanford reports (Apted, 1982; Apted and Myers, 1982; Wood et al., 1983; Myers et al., 1984a; Early et al., 1984) describe various premises that have been adopted by DOE-Hanford 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) (Myers et al., 1984a, p. 17).

2. Results of heat transfer calculations for various waste package configurations in an NWRB (Altenhofen 1981; Westinghouse-AESD, 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 (Myers et al., 1984a, p. 17).

3. The DOE-Hanford approach to hydrothermal testing of barrier materials is based on the concept of sequential penetration of barriers by intruding groundwater (Apted, 1982, pp. 162-163). 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 (Myers et al., 1984a, p. 1). This alteration will be manifested by nucleation and growth of an assemblage of secondary solid phases that is more stable than the primary phases (Apted, 1982, p. 164). Then, during the post-containment 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.

Geochemical processes near waste packages will be controlled or strongly influenced by the chemical reactivity of the waste form and nearby

barrier materials (Myers et al., 1984a, p. 1). 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 (Myers et al., 1984a, p. 35). 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 (Early et al., 1984, p. 162). 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 (Apted and Myers, 1982, p 71).

4. Migration of contaminated groundwater is the most credible mechanism of radionuclide transport (Myers et al., 1984a, p. 1). 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 (Apted, 1982, p. 162).

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 (Wood et al., 1983). Subsequent transport of dissolved radionuclides will occur down thermal gradients in the backfill and repository host rock (Early et al., 1984, p. 163). 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 (Early et al., 1984, p. 163).

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

The discussion items below, which are paraphrased from key DOE-Hanford reports (Apted, 1982; Apted and Myers, 1982; Wood et al., 1983; Myers et al., 1984a), describe premises which, taken together, comprise the philosophical framework of the DOE-Hanford 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 (Wood et al., 1983; Myers et al., 1984a, p. 6), 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, the DOE-Hanford program for hydrothermal testing of waste forms emphasizes measuring the "solubilities" (steady-state solubilities/concentrations) of radionuclides, not the leach rates of these elements (Apted, 1982, p. 164). 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 (Apted, 1982, p. 168).

2. In its program of hydrothermal testing of waste forms, DOE-Hanford 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 (Apted, 1982, p. 163). 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 (Apted and Myers, 1982, p. 68; Myers et al., 1984a, p. 68). 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 (Apted and Myers, 1982, p. 71). 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, DOE-Hanford staff members (Myers et al., 1984a) believe 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 (Apted and Myers, 1982, p. 68).

5. Performing experiments with simulated waste forms and obtaining measurements of the solubilities/concentrations of radionuclide-analog elements in simulated waste form + groundwater ± basalt systems constitute a preliminary basis for evaluating the radionuclide-containment

performances of fully radioactive waste forms (Myers et al., 1984a, p. 3). [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 (Myers et al., 1984a, p. 85). 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, DOE-Hanford has selected a standard pressure of 30 MPa for most of its hydrothermal experiments (Myers et al., 1984a, pp. 17-18). The only exception to this practice is the testing of DHLW borosilicate glass; for systems containing this simulated waste form, DOE-Hanford 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 (Apted, 1982, p. 169), and (2) results obtained at high temperatures can, in many instances, be extrapolated to low temperatures where time constraints may prohibit satisfactory experimental testing (Myers et al., 1984a, p. 17). Furthermore, data obtained from experiments performed at temperatures as high as 300°C are useful in modeling radionuclide-release scenerios 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-AESD, 1982), DOE-Hanford has selected 50 to 300°C as an appropriate temperature range for hydrothermal testing of barrier materials (Myers et al., 1984a, p. 17).

8. It is well known that rates of chemical reactions in rock-water experiments can be accelerated by fine grinding of solid starting materials (Apted, 1982, pp. 169-170). 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 (Myers et al, 1984a, p. 18).

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 (Myers et al., 1984a, p. 19).

3.2 REVIEW OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS

3.2.1 Experimental Results

This section presents: (1) summaries of DOE-Hanford information on the solubilities/concentrations of radionuclide-analog elements in simulated waste form ± Umtanum basalt + Grande Ronde groundwater systems at 90 to 300°C, and (2) an itemized listing of additional important information that DOE-Hanford 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 DOE-Hanford staff members and contractors (Apted and Myers, 1982; Myers et al., 1984a). Corresponding interpretations of these data by DOE-Hanford staff members and contractors — which occasionally 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.)

3.2.1.1 Key DOE-Hanford Information on the Solubilities of Radionuclide-Analog Elements at 90 to 300°C

3.2.1.1.1 Molybdenum

Non-radioactive 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 ± Umtanum basalt + GR-3 groundwater (P = 30 MPa, T = 100, 200, and 300°C) and simulated CHLW borosilicate glass ± Umtanum basalt + GR-A groundwater (P = 30 MPa, T = 100,

200, and 300°C) (Apted and Myers, 1982; Myers et al., 1984a).

1. The systems simulated spent fuel ± Umtanum basalt + GR-3 groundwater. 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 decrease systematically 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 ± Umtanum basalt + GR-A groundwater. Molybdenum is dissolved rapidly from CHLW borosilicate glass and, as was observed in 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-absent experiments were ~412, ~650, and ~1300 mg/L at 100, 200, and 300°C, respectively. Final concentrations of molybdenum in basalt-present experiments were ~69, ~161, and ~600 mg/L at 100, 200, and 300°C, respectively.)

3.2.1.1.2 Barium

Non-radioactive 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 ± Umtanum basalt + GR-3 groundwater (P = 30 MPa, T = 100, 200, and 300°C), simulated CHLW borosilicate glass ± Umtanum basalt + GR-A groundwater (P = 30 MPa, T = 100, 200, and 300°C), and simulated DHLW borosilicate glass + Umtanum basalt + GR-3 groundwater (Apted and Myers, 1982; Myers et al., 1984a).

1. The systems simulated spent fuel ± Umtanum basalt + GR-3 groundwater. Data for the system simulated spent fuel + GR-3 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 ± Umtanum basalt + GR-A groundwater. 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 0.04 to 0.12 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. The system simulated DHLW borosilicate glass + Umtanum basalt + GR-3 groundwater. At both 90 and 150°C, the concentration of barium rose at first, but subsequently declined significantly. Final concentrations were 0.037 mg/L (90°C) and 0.012 mg/L (150°C). Data obtained at 150°C suggest that the latter figure is a steady-state concentration.

3.2.1.1.3 Strontium

Non-radioactive strontium is a substitute for the radioactive isotopes of strontium (e.g., ^{90}Sr). Data on strontium have been obtained from experiments on the systems simulated spent fuel ± Umtanum basalt + GR-3 groundwater (P = 30 MPa, T = 100, 200, and 300°C), simulated CHLW borosilicate glass ± Umtanum basalt + GR-A groundwater (P = 30 MPa, T = 100, 200, and 300°C), and simulated DHLW borosilicate glass + Umtanum basalt + GR-3 groundwater (P = 10 MPa, T = 90 and 150°C) (Apted and Myers, 1982; Myers et al., 1984a).

1. The systems simulated spent fuel ± Umtanum basalt + GR-3 groundwater. In the system simulated spent fuel + GR-3 groundwater, the concentration of strontium decreased erratically during experimentation (from ~0.16 to ~0.05 mg/L at 100°C, from ~0.02 to ~0.01 mg/L at 200°C, and from ~0.09 to ~0.01 mg/L at 300°C). In experiments performed on the system simulated spent fuel + Umtanum basalt + GR-3 groundwater at 200 and 300°C, strontium concentrations increased at first, but thereafter gradually returned to their initial values (initial and final concentrations were ~0.3 and ~0.2 mg/L at 200 and 300°C, respectively). At 100°C, the behavior of strontium in this system was similar to that

observed at 200 and 300°C, the only significant difference being that, while Sr concentrations declined toward the end of experimentation, they did not decrease as much as at 200 and 300°C (the final concentration was 2.1 mg/L).

2. The systems simulated CHLW borosilicate glass ± Umtanum basalt + GR-A groundwater. In experiments performed on the system simulated CHLW borosilicate glass + GR-A groundwater at 200 and 300°C, strontium concentrations rose from initial values of 0 mg/L to apparent steady-state concentrations of ~0.01 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 + Umtanum basalt + GR-A groundwater. At 200 and 300°C, strontium concentrations rose from initial values of 0 mg/L to ~0.02 mg/L. 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.

3. The system simulated DHLW borosilicate glass + Umtanum basalt + GR-3 groundwater. 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 near the end of the experiment (the final measured concentration was 0.018 mg/L).

3.2.1.1.4 Cesium

Non-radioactive 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 + Umtanum basalt + GR-3 groundwater (P = 30 MPa, T = 100, 200, and 300°C) (Apted and Myers, 1982; Myers et al., 1984a).

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.

3.2.1.1.5 Iodine

Non-radioactive 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 ± Umtanum basalt + GR-3 groundwater (P = 30 MPa, T = 100, 200, and 300°C) (Apted and Myers, 1982; Myers et al., 1984a).

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 DOE-Hanford 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.

3.2.1.1.6 Uranium

Data on uranium have been obtained from experiments on the system simulated spent fuel ± Umtanum basalt + GR-3 groundwater (P = 30 MPa, T = 100, 200, and 300°C) (Myers et al., 1984a).

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.

3.2.1.2 Additional Significant Experimental Information

The discussion items below, which are paraphrased from key DOE-Hanford reports (principally Apted and Myers, 1982, and Myers et al., 1984a), describe some additional important experimental results obtained by DOE-Hanford staff members and contractors.

1. Compositional and structural differences between simulated spent fuel and borosilicate glass are reflected in the significantly different hydrothermal reactivities of these two waste forms (Myers et al.,

1984a, p. 81). In general, the major elements of simulated spent fuel are sparingly soluble in synthetic groundwater (Myers et al., 1984a, p. 45). 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 (Apted and Myers, 1982, p. 71-72). In particular, the solubilities of Si, Na, B, and Mo are much higher in borosilicate glass ± Umtanum basalt + Grande Ronde groundwater systems than in simulated spent fuel ± Umtanum basalt + Grande Ronde groundwater systems. This observation is partly attributable to the fact that different primary and secondary solid phases control or influence the groundwater "solubilities" of nuclides 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 (Apted and Myers, 1982, p. 69). The presence of significant amounts 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 + GR-3 groundwater is to <u>increase</u> the amounts of dissolved Si and K; the concentrations of other

solute elements remain more or less unchanged (Myers et al., 1984a, p. 69). By contrast, for borosilicate-glass systems, the principal effect of adding basalt is to decrease the concentrations of Si, Na, and B (Myers et al., 1984a, p. 73). Comparing the results obtained from experiments on simulated spent fuel ± Umtanum basalt + Grande Ronde groundwater systems with corresponding results obtained from experiments on borosilicate glass ± Umtanum basalt + Grande Ronde groundwater systems, it is evident that, in particular, the solubilities/concentrations of Si, Na, B, and Mo are much higher in the borosilicate glass systems (Myers et al., 1984a, p. 81). 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 (Apted and Myers, 1982, p. 58). 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 simulated waste form ± Umtanum basalt + Grande Ronde groundwater 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 (Myers et al., 1984a, p. 44). Consequently, saturation of groundwater with silicon (or any other non-radioactive element) does not preclude subsequent release (dissolution) of radionuclides from a waste form as has been hypothesized by some investigators (Myers et al., 1984a, p. 64).

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 (Myers et al., 1984a, p. 44; Grandstaff et al., 1984).

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 (Myers et al., 1984a, pp. 41-42). 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 simulated waste form ± Umtanum basalt + Grande Ronde groundwater 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 either be higher or lower than the pH that is measured at 25°C (Myers et al., 1984a, p. 49).

7. According to calculations performed with the computer code HIPH4 (Apted and Myers 1982, pp. 15-17; Myers et al., 1984a, pp. 27-28), at $T < 100°C$ the pH of groundwater in the system basalt + groundwater is controlled by the silicic acid and bicarbonate buffers, while at $T > 100°C$ the dissociation of water is the predominant pH buffering reaction (Myers et al., 1984a, p. 30). However, the results of 25°C pH measurements on synthetic groundwaters obtained from simulated waste

form ± Umtanum basalt + Grande Ronde groundwater experiments indicate that simulated waste forms may significantly influence pH during experimentation. For example, Apted and Myers (1982, p. 38) and Myers et al. (1984a, p. 45) suggest that, at 300°C, simulated spent fuel reacts with Umtanum basalt and GR-3 groundwater in a manner that causes pH to decrease. Also, 25°C pH data described by Apted and Myers (1982) and Myers et al. (1984a) indicate that, among other effects, the dissolution of borosilicate glass causes pH to rise to levels above those achieved in basalt + groundwater experiments (Apted and Myers, 1982, p. 71).

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 + Umtanum basalt + GR-3 groundwater suggest that changes in the concentration of CO_3^{2-} during experimentation were influenced by the initial grain size of the basalt (Myers et al., 1984a, p. 33). 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 + Umtanum basalt + GR-3 groundwater, 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 (Myers et al., 1984a, p. 65).

3.2.2 Calculational Results

To date, there is no evidence of attempts by DOE-Hanford 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 DOE-HANFORD-CITED LIMITATIONS OF DOE-HANFORD "SOLUBILITY" INFORMATION

Apted and Myers (1982) and Myers et al. (1984a) cite the following important limitations of DOE-Hanford experimental data on the solubilities of radionuclides and radionuclide-analog elements at 90 to 300°C.

1. The synthetic groundwaters used in hydrothermal experiments performed by DOE-Hanford 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 (Myers et al., 1984a, p. 68). These differences are likely because, before they are able to contact radioactive waste, the groundwaters in an NWRB must first pass through hydrothermally altered basalt and a series of engineered barrier materials. Groundwaters flowing along such paths will experience increases in temperature as the radioactive waste is approached and, therefore, it is to be expected that the chemistries of these groundwaters will be modified extensively by reactions with transgressed solid materials.

2. Methods have not yet been devised to directly or indirectly measure groundwater Eh (redox potential) in barrier materials + groundwater experiments performed at temperatures above 100°C (however, see Myers et al., 1984b).

3. Calculated pHs for groundwaters in barrier materials + groundwater systems at temperatures above 100°C are of uncertain accuracy owing 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 (Myers et al., 1984a, p. 28).

3.4 ASSESSMENT OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES/ CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS

This section contains various comments by the author concerning DOE-Hanford information on the solubilities/concentrations of radionuclides and radionuclide-analog elements in barrier materials + groundwater systems at 90 to 300°C.

1. Concentration-vs-time behavior of solute elements — Collectively, the data obtained to date from closed, isobaric, isothermal, simulated waste form ± Umtanum basalt + Grande Ronde groundwater experiments indicate that the solubilities/concentrations of individual solute elements (including radionuclides and radionuclide-analog elements) 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 cessation of experimentation, while in the same experiment 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 variable amounts of suspended material (particulates and colloids) 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 nuclide sorption by mineral crystalline solutions — The effects of solid-phase dissolution and precipitation on the "solubilities" of nuclides are discussed at length in DOE-Hanford publications, but the potentially significant effects of sorption 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 and radionuclide-analog elements. Furthermore, in certain circumstances, sorption by mineral crystalline solutions can forestall or preclude the precipitation/crystallization of discrete radionuclide-rich or radionuclide-analog-element-rich solid phases.

3. The effects of waste-form composition on data obtained from barrier materials + groundwater experiments — It would be useful to investigate the possibility that data obtained from simulated waste form ± basalt + groundwater experiments can be affected significantly by relatively

small changes in the composition of the simulated waste form. In particular, it would be important to determine whether or not the solubilities/concentrations of radionuclides and radionuclide-analog elements can be altered significantly by such changes.

4. The use of freshly ground basalt in barrier materials + groundwater experiments — The use of freshly ground basalt as a solid starting material in barrier materials + groundwater experiments would seem to be ill-advised because the crushed basalt in the packing material of waste packages in 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.

5. Precision of radionuclide solubility data — Determinations of the true characteristics and significance of hydrothermal data on the solubilities/concentrations of 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 feasible to do so — or (at least) estimated empirically.

6. Some comments concerning "the Volkswagen diagram" — There are three confusing aspects of Figure 2 in Apted (1982), which is reproduced here in Fig. 1. (For reasons that 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 DOE-Hanford

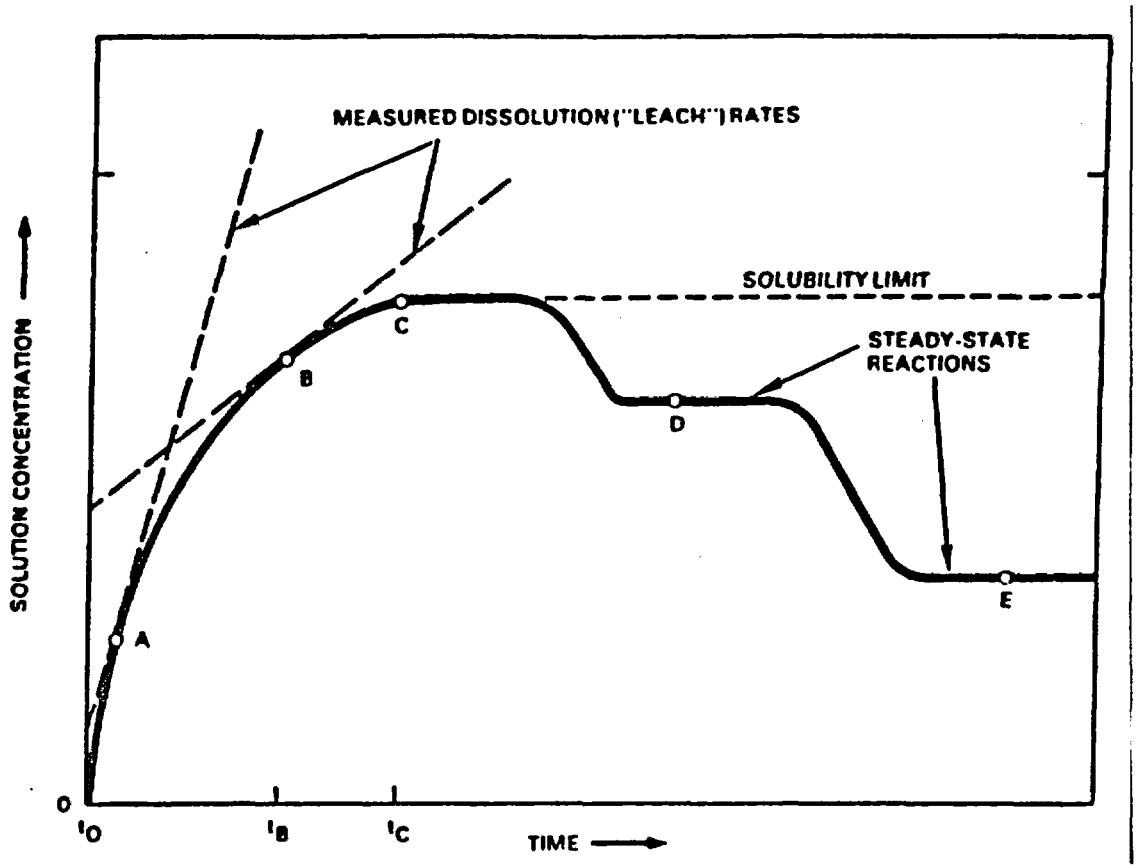

Fig. 1. Schematic illustration of solution concentration as a function of time for a hypothetical barrier materials + groundwater system.

Source: Apted, M. J., Overview of Hydrothermal Testing of Waste Package Barrier Materials at the Basalt Waste Isolation Project, PNL-4382, Pacific Northwest Laboratory, Richland, Washington, 1982.

staff members are claiming is a general rule-of-thumb concerning the concentration-vs-time behavior of dissolved radionuclides in barrier materials + groundwater systems.

First, Apted does not indicate specifically that the figure refers to reactions/equilibria in a closed, isobaric, isothermal system.

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 nearly 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., 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 postcontainment 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. It is true that a closed, multi-solid-phase hydrothermal system will, with time, evolve toward lower total free energy states as highly metastable phase assemblages are converted to

less metastable assemblages. However, the amounts of dissolved radionuclides in such a system 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 statement 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 sorbed trace components.

Experimental evidence that supports these assertions includes the data that DOE-Hanford has obtained on the concentration-vs-time behavior of cesium in an experiment performed on the system simulated spent fuel + Umtanum basalt + GR-3 groundwater at 300°C. During this experiment — run BSF-3 described by Myers et al. (1984a, Figure A-8) — the concentration of cesium, initially ~3 mg/L, increased sharply to ~48 mg/L after 1 h, remained nearly constant through 3 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 to the presence of variable quantities of cesium-bearing particulates and/or colloids in the synthetic groundwaters, it may be concluded 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 nuclide will thereafter always either remain constant or continuously decrease with increasing time.

7. Some consequences of using different synthetic groundwaters and different analytical methods in barrier materials + groundwater experiments — It is unfortunate that DOE-Hanford staff members and contractors have used two different types of synthetic groundwaters (GR-3 and GR-A) in their simulated waste form ± Umtanum basalt + Grande Ronde groundwater experiments. 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 simulated waste form ± Umtanum basalt + Grande Ronde groundwater systems.

8. Some comments on measured and calculated values of pH for synthetic groundwaters — Calculated pHs for synthetic groundwaters at high temperatures in the systems simulated spent ± Umtanum basalt fuel + GR-3 groundwater and simulated CHLW borosilicate glass ± Umtanum basalt + GR-A groundwater are of highly uncertain accuracy. Until there is some means of validating the accuracy of these calculated pHs, no particular significance should be lent to them.

4. DOE-HANFORD INFORMATION ON THE SOLUBILITIES OF RADIONUCLIDE-ANALOG ELEMENTS AT 1 ATM, 25 TO 90°C

4.1 DOE-HANFORD APPROACH TO DATA DEVELOPMENT

The discussion items below, which are paraphrased from commentary in Early et al. (1982) and Early et al. (1984), describe various premises that Early et al. adopted concerning calculated solubilities for radionuclide-analog elements at 1 atm, 25 to 60°C.

1. "Baseline" calculations of the solubilities of radionuclide-analog elements at 25°C can be performed using published thermodynamic data for aqueous radionuclide-analog-element species and radionuclide-analog-element 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 recognized, however, that laboratory tests will be required to confirm the accuracies 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 radionuclide-analog elements are influenced by the Eh, pH (redox conditions), and composition of groundwater, calculations of the solubilities of radionuclide-analog elements should be performed using ranges of values for these

geochemical parameters. The ranges of Eh, pH, and groundwater composition that are investigated should encompass the values that have been measured or are expected to exist in the various basalt-groundwater systems in the NWRB. This calculational approach offers two advantages: (1) the sensitivities of the solubilities of radionuclide-analog-elements to Eh, pH, and groundwater chemistry can be evaluated, and this information can be used to determine the degree to which Eh, pH, and groundwater chemistry must be known in order to accurately predict the solubilities of radionuclide-analog elements 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.

According to Early et al. (1984), the Ehs and pHs of Grande Ronde groundwaters are fairly constant, but groundwater chemistry is rather variable. Measured Ehs for Grande Ronde groundwaters, which are frequently 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, it has been estimated that the "true" Eh of groundwaters in Grande Ronde basalts is -0.40 ± 0.05 V at 57 ± 2°C (DOE, 1982). Measured pHs 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 DOE-Hanford geochemists through chemical analyses performed on 29 different samples of Grande Ronde groundwater obtained from five separate

wells on the Hanford Reservation. [Note: 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 the 29 different samples of Grande Ronde groundwater, nor do they indicate which reaction or reactions are most influential in establishing and maintaining the high pHs of these groundwaters.]

4. The presence of SO_4^{2-} in Grande Ronde groundwaters, and the evidence suggesting relatively reducing (low oxidation potential) conditions in Grande Ronde basalts, indicate that the potential effects of sulfate-sulfide equilibration should be explored in calculations of radionuclide speciation and solubility in Grande Ronde groundwaters (Early et al., 1984). Although aqueous sulfide species (S^{2-} and HS^-) have not yet been detected in Grande Ronde groundwaters* (Gephart et al., 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 radionuclide-analog elements 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 nuclides to very low values. For these reasons, it is useful to investigate how groundwater speciation and solubilities of

---

*Subsequent to the study conducted by Early et al. (1984), small quantities of S^{2-} and HS^- were detected in various Grande Ronde groundwaters (DOE, 1986, p. C.5-82).

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

Element/ radionuclide	Solubility-limiting solids and dominant aqueous species: Solubility-limiting solid	Solubility-limiting solids and dominant aqueous species: Dominant aqueous species	Computed solubilities: Solubility range in Grande Ronde groundwaters (mol/L)	Computed solubilities: Solubility in GR-3 synthetic Grande Ronde groundwater (mol/L)	Solubility estimates from experiments and natural Grande Ronde groundwaters (mol/L)
Ni	NiO	$NiCO_3^0$	$4 \times 10^{-5} - 3 \times 10^{-3}$	2×10^{-4}	$>10^{-6}$[a]
	$Ni(CO_3)_2^{2}$				
Se	Se	NSe	$1 \times 10^{-8} - 5 \times 10^{-7}$	6×10^{-8}	$\sim 10^{-6}$[b]
Zr	$ZrSiO_4$	$Zr(OH)_5$	$1 \times 10^{-10} - 2 \times 10^{-8}$	2×10^{-9}	--
Pd	Pd	$NiCO_3^0$	$2 \times 10^{-12} - 4 \times 10^{-9}$	2×10^{-10}	
Sn	SnO_2	$SnO(OH)^+$			
		$SnO(OH)_2^0, Sn(OH)_3$	$4 \times 10^{-19} - 2 \times 10^{-17}$	2×10^{-18}	
Sb	$Sb(OH)_3$	$Sb(OH)_3^0$	$1 \times 10^{-7} - 2 \times 10^{-7}$	1×10^{-7}	
Sm	$Sm(OH)_3$	$Sm(OH)_3^0, Sm(OH)_4$			
		$Sm(OH)_3^{+3}, Sm(OH)_2^+$			
Eu	$Eu(OH)_3$	$Eu(OH)_4^-, Eu(OH)_3^0$	$3 \times 10^{-9} - 5 \times 10^{-8}$	3×10^{-9}	
		$EuCO_3^+, Eu(OH)_2^{+3}$			
Pb	$Pb(OH)_2$	$PbCO_3^0$	$7 \times 10^{-9} - 7 \times 10^{-7}$	3×10^{-8}	$>10^{-7}$[a]
		$Pb(CO_3)_2^{2-}$			
Th	ThO_2	$Th(OH)_4^0$	8×10^{-15}	8×10^{-15}	$<10^{-8}$[b]
U	$USiO_4$	$U(OH)_5$	$2 \times 10^{-11} - 2 \times 10^{-9}$	2×10^{-10}	$>10^{-9}$[a]
Np	NpO_2	$Np(OH)_5$	$2 \times 10^{-11} - 7 \times 10^{-10}$	1×10^{-10}	10^{-6}[b]
Pu	PuO_2	$Pu(OH)_5^-$[c]	$5 \times 10^{-12} - 1 \times 10^{-6}$[c]	8×10^{-10}[c]	
		$PuCO_3^{2+}$[d]	$4 \times 10^{-14} - 2 \times 10^{-12}$[d]	3×13^{-10}[d]	
Am	$Am(OH)_3$	$Am(CO_3)_2, Am(CO_3)_3^{3-}$	$4 \times 10^{-9} - 1 \times 10^{-6}$	2×10^{-8}	$10^{-9} - 10^{-8}$[e]
		$AmCO_3^+$			

[a]From maxium concentration levels observed in Hanford groundwaters.
[b]From sorption experiments.
[c]Solubilities based upon published stability constant for $PuCO_3^{2+}$ complex.
[d]Solubilities based upon absence of $PuCO_3^{2+}$ complex.
[e]Edelstein et al. (1983).

Source: Early, T. O., G. K. Jacobs, and D. R. Drewes, "Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt," Am. Chem. Soc. Symp. Ser. 246, 147-166, Table 11, 1984.

radionuclide-analog elements are affected by forming or not forming reduced aqueous sulfide species and solid sulfide precipitates (Early et al., 1984).

4.2 REVIEW OF PUBLISHED DOE-HANFORD SOLUBILITY INFORMATION

4.2.1 Experimental Results

To the author's knowledge, there are no DOE-Hanford documents published as of July 1, 1986, which describe DOE-Hanford experiments on the solubilities of radionuclides at "low" temperatures (25 to 90°C). However, a limited quantity of solubility data obtained from DOE-Hanford sorption experiments are presented by Early et al. (1984, Table II) (see Table 1).

4.2.2 Calculational Results

Early et al. (1984) have calculated solubilities for radionuclide-analog elements in Grande Ronde groundwaters at 25°C using: (1) $\Delta G^{\circ}_{f,298K}$ 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 and Morgan, 1981). The major goals of the calculations were to determine how calculated solubilities of radionuclide-analog elements would be affected by: (1) variations in Eh and pH, (2) variations in Grande Ronde groundwater chemistry, and (3) constraints on equilibria among aqueous sulfur species.

The effects of Eh on calculated solubilities of radionuclide-analog elements 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 radionuclide-analog elements 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 calculated solubilities is due, either directly or indirectly, to the different pHs of the groundwaters. Early et al. (1984) also state that computed solubilities of radionuclide-analog elements were not affected significantly by different concentrations of F^-, Cl^-, SO_4^{2-} and SiO_2° in the groundwaters.

The effects of constraints on equilibria among aqueous sulfur species were investigated using the GR-3 groundwater composition (Jones, 1982). Calculations were performed for various radionuclide-analog elements 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 Ehs, 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, at the time that Early et al. were performing their calculations, S^{2-} and HS^- had not yet been detected in Grande Ronde groundwaters. The reference value of Eh for the calculations is -0.3 V. Early et al. state that this value is approximately midway between the theoretical estimate of Eh for basalt/groundwater equilibrium (-0.40 V) and the average of measured Ehs 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 precipitates 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 nuclides.

Examination of the data presented in Table 1 leads to several significant conclusions (Early et al., 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 (e.g., PO_4^{2-}) that could

potentially form strong complexes with many of the radionuclide-analog elements. Solids that control the solubilities of the radionuclide-analog elements 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 firmly established that the solubilities of radionuclide-analog elements can be 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 radionuclide-analog elements.

4.3 DOE-HANFORD-CITED LIMITATIONS OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES OF RADIONUCLIDE-ANALOG ELEMENTS

The discussion items below, which are paraphrased from commentary in Early et al. (1982) and Early et al. (1984), describe important limitations of DOE-Hanford calculations of the solubilities of radionuclide-analog elements at 1 atm, 25 to 90°C.

1. Calculated stabilities of aqueous radionuclide-analog-element species and coexisting radionuclide-analog-element-bearing solid phase — which yield calculated solubilities for radionuclide-analog elements — 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-analog-element-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 solubilities that are erroneously high. On the other hand, if thermodynamic data are unavailable for aqueous complexes that are more stable than those represented in the data base, then calculated solubilities of radionuclide-analog elements 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 radionuclide-analog elements. No attempt was made 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, no attempt was made to determine how calculated solubilities of radionuclide-analog elements are affected by statistically determined uncertainties for the thermodynamic data.

2. Solubilities of radionuclide-analog elements were calculated for 25°C, whereas measured temperatures of groundwaters in Grande Ronde basalts range from 48 to 59°C (Long and WCC, 1984). The inability to perform accurate calculations for a 48 to 59°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 solubilities of radionuclide-analog elements for 48 to 59°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 radionuclide-analog elements, but these increases are not expected to be larger than one order of magnitude.

3. The calculations are partly based on the assumption that the solubilities of radionuclide-analog elements are controlled by <u>the most stable solid phases of fixed composition.</u> If, instead, the solubilities of radionuclide-analog elements 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 the calculations. Also, because the calculations are based on the assumption that solid phases (and particularly radionuclide-analog-element-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). Also, a radionuclide-analog-element-rich solid solution phase may precipitate even if there are more stable "pure" solid phases for one or more of the radionuclide-analog elements. 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 were not taken into account in the calculations of the groundwater solubilities of radionuclide-analog elements.

4.4 ASSESSMENT OF DOE-HANFORD INFORMATION ON THE SOLUBILITIES OF RADIONUCLIDE-ANALOG ELEMENTS

Discussions presented by Early et al. (1984) indicate that DOE-Hanford is well aware of the limitations of its information on the solubilities of radionuclide-analog elements in Grande Ronde groundwaters at "low" temperatures (25 to 60°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. <u>The use of calculated radionuclide solubilities to estimate radionuclide source terms</u>. It is significant that calculated solubilites of radionuclide-analog elements at "low" temperatures are frequently many of orders magnitude lower than corresponding measured solubilities

obtained from hydrothermal experiments performed at "high" temperatures. The indication that the solubilities of radionuclide-analog elements 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. According to Early et al. (1984), one of the reasons that calculated solubilities of radionuclide-analog elements are apt to be 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 the solubilities of radionuclide-analog elements are often controlled by metastable radionuclide-analog-element-rich solid phases for which there are no available thermodynamic data. For this reason, it may be advisable to treat solubilities calculated from thermodynamic data as minimum values for the solubilities which are selected to estimate radionuclide source terms in an NWRB.

2. Lack of information on the solubilities of radionuclide-analog elments at "low" temperatures. Unfortunately, there is very little information available on the experiments that DOE-Hanford staff members and contractors have performed on the solubilities of radionuclide-analog elements at 25 to 60°C. A small amount of data obtained from these experiments has been presented by Early et al. (1984, Table II) (see Table 1).

3. Treating Eh as an independent variable. In their solubility calculations, Early et al. (1982) and Early et al. (1984) treat Eh as an independent variable. The problem with this approach is that, in both natural and synthetic rock-groundwater systems, Eh is really not an independent variable. Rather, in these systems, which are typically rock dominated, Eh is a dependent variable 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 (Kelmers et al., 1985) 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 et al., 1983).

• Nickel. Assuming no SO_4^{2-} speciation (reduction) to S^{2-} and HS^- ions, the calculations performed with MINTEQ indicate that $Ni(OH)_2$, 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 $Ni(OH)_2$. In the MINTEQ data base, $\log K_f = -10.8$ for $Ni(OH)_2$, whereas in the data base employed by Early et al., $\log K_f = -12.7$ (Benson and Teague, 1980). When sulfate speciation to S^{2-} and HS^- ions is permitted in the calculations, the calculations performed with MINTEQ again indicate that $Ni(OH)_2$ 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. These conflicting 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, $\log K_f = 41.7$, whereas in the data base used by Early et al., $\log K_f = 47.3$.

5. A SUMMARY OF DOE-HANFORD DATA ON THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS IN BARRIER MATERIALS + GROUNDWATER SYSTEMS

Published DOE-Hanford data on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems are here summarized in five separate tables — Tables 2-6 — one table for each of the five major types of systems that have been investigated experimentally. The data listed in Tables 2-5 are solubilities/concentrations derived from hydrothermal experiments performed at 100, 200, and 300°C. The data listed in Table 6 are solubilities/concentrations derived from experiments performed at 90 and 150°C. In each table, the data for individual radionuclide-analog elements are divided according to the temperature at which they were obtained. Individual columns of numbers compare two separate sets of data: (1) solubilities/concentrations listed by Myers et al. (1984a), and (2) solubilities/concentrations generated by the author via his own independent assessment of the data presented by Myers et al. (1984a).

5.1 THE RATIONALE FOR SEGREGATING THE SOLUBILITY/CONCENTRATION DATA BY SYSTEM AND TEMPERATURE

Before discussing the results presented in Tables 2-6, the author wishes to defend his decision to employ five separate tables to summarize DOE-Hanford hydrothermal data on the solubilities/concentrations of radionuclide-analog elements. First, it should be recognized that this approach is consistent with the format of discussions presented in Sect. 3 of the present report. The reader will recall that Sect. 3 dealt with DOE-Hanford experimental data on the solubilities/concentrations of radionuclide-analog elements at 10 to 30 MPa, 90 to 300°C, and in this

Table 2. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated spent fuel + GR-3 groundwater[a]

Element	Temperature ⟶	100°C	200°C	300°C
	Run # ⟶	D6-8	D6-1	D5-1
Ba		0.18[b](~0.3[b])	0.12[b](~0.12[b])	0.03[b](~0.05[b])
Mo		71[b](~80[b])	68[b](~68[b])	150[b](136)
Sr		0.04[b](~0.05)	0.01[b](0.01)	0.007[b](~0.008[b])

[a]The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984a, Figures A-2, A-3, and A-4). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984a, Table 8-2) (see Table B.1 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984a, Figures A-2, A-3, and A-4).

[b]Judged to be a steady-state solubility/concentration.

Table 3. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated spent fuel + Umtanum basalt + GR-3 groundwater[a]

Element	Temperature ⟶	100°C	200°C	300°C
	Run # ⟶	BSF-4	BSF-2	BSF-3
Ba		1.0[b](0.0-3.5)	<0.03[b](~0)	<0.03[b](0.0-1.3)
Cs		50.0[b](~50[b])	30.5[B](~30[b])	46.8[b](46.8)
I		11.0[c](~11.0[c])	0.04(?)	11.2[c](~11[c])
Mo		75[b](~75[b])	76[b](~49)	18.9[b](18.9)
Sr		2.1[b](~2[b])	0.36[b](~0.3[b])	0.21[b](0.2)
U		0.29[b](~0.3[b])	0.10[b](~0.1)	0.13[b](0.1[b])

[a]The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984a, Figures A-5, A-6, and A-8). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984a, Table 8-2) (see Table B.2 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984a, Figures A-5, A-6, and A-8).

[b]Judged to be a steady-state solubility/concentration.

[c]Judged to be an inventory-limited concentration.

Table 4. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated CHLW borosilicate glass + GR-A groundwater[a]

Element	Temperature ⟶	100°C	200°C	300°C
	Run # ⟶	GLSW 3-1	GLSW 2-1	GLSW 1-2
Ba		1.27[b](1.08)	0.03[b](0.04)	0.18[b](0.12)
Mo		188[b](412)	650[b](650[b])	1290[c](1300[c])
Sr		0.89[b](0.73)	0.004[b](0.1[b])	0.04[b](0.04)

[a]The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984a, Figures A-10, A-12, and A-14). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984a, Table 8-2) (see Table B.3 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984a, Figures A-10, A-12, and A-14).

[b]Judged to be a steady-state solubility/concentration.

[c]Judged to be an inventory-limited concentration.

Table 5. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated CHLW borosilicate glass + Umtanum basalt + GR-A groundwater[a]

Element	Temperature ⟶	100°C	200°C	300°C
	Run # ⟶	BGLW 3-1	BGLW 2-1	BGLW 1-1
Ba		0.47[b](0.47)	0.07[b](~0.06[b])	0.06[b](0.06)
Mo		69[b](69)	161[b](161)	620[c](~600[c])
Sr		0.28[b](0.28)	0.02[b](0.02[b])	0.02[b](~0.01)

[a]The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984a, Figures A-15, A-16, and A-17). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984a, Table 8-2) (see Table B.4 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984a, Figures A-15, A-16, and A-17).

[b]Judged to be a steady-state solubility/concentration.

[c]Judged to be an inventory-limited concentration.

Table 6. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated DHLW borosilicate glass + Umtanum basalt + GR-3 groundwater[a]

Element	Temperature ⟶	90°C	150°C
	Run # ⟶	D7-1	D8-1
Ba		0.037[b](0.037)	0.012[b](0.012[b])
Sr		0.006[b](~0.005[b])	0.018[b](0.018)

[a]The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984a, Figures A-21 and A-23). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984a, Table 8-2) (see Table B.5 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984a, Figures A-21 and A-23).

[b]Judged to be a steady-state solubility/concentration.

section the discussions of experimental data were segregated according to system and temperature. The discussions were segregated by system because it is now known that the solubilities/concentrations of numerous radionuclide-analog elements are strong functions of bulk composition, and the five barrier materials + groundwater systems that have been investigated by DOE-Hanford to date are sufficiently different in bulk composition to warrant separate listings of data for each system. Subdividing the data by temperature is also justified, because the available solubility/concentration data have been obtained at temperatures that are sufficiently widely spaced to reveal the effects of temperature on solubility/concentration.

5.1.1 Potential Difficulties in Continuing to Classify Solubility/Concentration Data by System and Temperature

Classifying DOE-Hanford solubility/concentration data by system and temperature is satisfactory for the present time because only a small number of bulk compositions and temperatures have been investigated. However, should numerous additional simulated waste forms be investigated experimentally in the future, classification of solubilities/concentrations by system will become increasingly complicated and cumbersome. This is so because, instead of a single number for the solubility/concentration of a nuclide in a given system at a given temperature, there will be a range of solubilities/concentrations.* Furthermore, it is distinctly possible that the solubilities/concentrations of some nuclides will vary markedly with relatively small changes in bulk composition. For these nuclides,

categorization of solubility/concentration by system and temperature would no longer be satisfactory; instead, it would be necessary to specify solubility/concentration by bulk composition and temperature.

It is also possible that future DOE-Hanford experimental studies will further elucidate the effects of temperature on the solubilities/concentrations of radionuclide-analog elements. If so, then tables similar to Tables 2-6 would have to include many additional columns to

---

*This statement is based on the assumption that DOE-Hanford staff members will continue to classify their experimentally-based solubility/concentration data as they have done in the past; viz., according to the "generic" barrier materials(s) present in a given system (e.g., "spent fuel," "CHLW glass," "DHLW glass," "basalt," etc.). Of course, DOE-Hanford may eventually decide to further classify their solubility/concentration data in order to be more specific about the particular bulk compositions to which the data apply. For example, instead of classifying their experimentally-based solubility/concentration data on the basis of whether a system contains a particular general type of waste form (e.g., "spent fuel"), DOE-Hanford may decide to divide such systems into subsystems that would draw finer distinctions between the types of waste forms employed in experimentation (e.g., "H. B. Robinson spent fuel + ... + ... groundwater," "Turkey Point spent fuel + ... + ... groundwater," and so on). This method of classification would narrow the range of bulk compositions covered by a particular type of system, thereby making it more likely that a single number would be satisfactory for representing the solubility/concentration of a particular nuclide in a given system at a given temperature. However, a proliferation of systems is still no guarantee that this simplification can be achieved. This is so because a waste form of a given "origin" (e.g., spent fuel from a particular reactor) can still be physically or chemically heterogeneous and, furthermore, its particular physicochemical characteristics may depend on its "history" and "age" (e.g., for spent fuel, the degree of "burn-up," and the length of time it has been out of the reactor). Therefore, unless DOE-Hanford decides to segregate its solubility/concentration data into a very large number of systems (i.e., a different system for each barrier material of slightly different bulk composition and/or physicochemical make-up), it will probably be necessary to list a range of solubilities/concentrations for one or more nuclides in a particluar system at a given temperature.

properly document all of the variations in solubility/concentration with temperature. If these variations are found to be a sensitive function of bulk composition, then it is evident that a large number of tables would be required to list all of the available information.

Finally, eventually it may be necessary or desirable to develop mathematical functions to represent the solubility/concentration data. With small amounts of data, this task is readily accomplished by the usual methods of empirical mathematical fitting (e.g., least-squares regression analysis). However, as the quantity of solubility/concentration data increases, empirical mathematical fitting becomes increasingly cumbersome. This realization is one of the principal motivating factors behind the effort to develop geochemical computer codes that provide accurate calculated solubilities/concentrations of nuclides in barrier materials + groundwater systems.

5.2 ADDITIONAL COMPLEXITIES IN EXPERIMENTAL MEASUREMENTS OF THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS

Unfortunately, complexities in experimental measurements of the solubilities/concentrations of radionuclide-analog elements are not limited to the complications that stem from the effects of bulk composition and temperature. In addition to these two factors, it is evident from the discussions presented in Sect. 3 that the solubilities/concentrations of many radionuclide-analog elements are also a function of time. Time is a significant parameter because barrier materials + groundwater systems are often highly unstable thermodynamically and,

therefore, they frequently exhibit rapid initial solid/fluid interaction. (Accordingly, in these highly reactive system, the solubilities/concentrations of nuclides tend to change rapidly at first.) However, after a few tens or hundreds of hours, it is typically observed that: (1) solid/fluid reaction rates diminish or become counterbalancing, and (2) nuclide solubilities/concentrations begin to stabilize. If the solubility/concentration of a given nuclide eventually becomes nearly constant with time, then the concentration is said to be at a "steady state." Significantly, one of the principal stated goals of DOE-Hanford hydrothermal experimentation is to delineate the steady-state concentrations of radionuclides and radionuclide-analog elements in barrier materials + groundwater systems.

However, there are several difficulties associated with measuring and interpreting steady-state concentrations of radionuclides and radionuclide-analog elements. First, as discussed more thoroughly below, it can be a matter of judgment whether or not a given set of solubility/concentration data truly establish that steady-state conditions have been achieved. Two factors are key in this regard: (1) the quantity and "distribution" of solubility/concentration data, and (2) the accuracy and precision of the solubility/concentration data. The first factor refers to the number of times that groundwater is sampled and analyzed during experimentation, and to the intervals of time between sampling. To determine that a given nuclide has achieved a steady-state concentration, it is necessary to show that the concentration of the nuclide has remained nearly constant for a

significant period of time. This determination is facilitated by sampling frequently at regularly spaced intervals of time. (Transient steady states may go undetected if samples are taken infrequently or at irregularly spaced intervals.) The accuracy and precision of solubility/concentration data is another key factor in detecting steady-state conditions, because excessive "scatter" in the data can make it difficult to establish that these conditions have, in fact, been achieved.

It is also evident from the discussions presented in Sect. 3 that there can be more than one steady state for a nuclide in a closed-system experiment at a constant pressure and temperature. One of the key factors in this regard is duration of experimentation. The DOE-Hanford data obtained to date suggest that, the longer an experiment is allowed to continue, the more likely it is that temporary kinetic or thermodynamic balances will be achieved. Therefore, the total number of steady states observed during an experiment, as well as the concentrations of nuclides measured at the end of the experiment, can be highly dependent on the duration of experimentation.

The reactivities and evolutionary histories of barrier materials + groundwater systems are also influenced by the initial physical states of solid starting materials. The potential importance of the initial physical characteristics of solid starting materials is well exemplified by the different reactivities of real spent fuel and simulated spent fuel. Real spent fuel is dense (sintered) and, therefore, it is little

altered during hydrothermal experimentation (Thomas et al., 1985). By contrast, simulated spent fuel is an unconsolidated admixture of several physically discrete chemical constituents and, therefore, compared to real spent fuel, it is highly reactive with groundwater (Myers et al., 1984a; Grandstaff et al., 1984).

The particular results obtained in experiments can also be profoundly affected by fine-grinding of solid starting materials, as Myers et al. (1984a) discovered in their experiments on the system simulated spent fuel + Umtanum basalt + GR-3 groundwater. In general, much more rapid reaction rates (and, hence, much more rapid approaches to steady-state conditions) are achieved when solid starting materials are comminuted to small grain sizes. However, along with more rapid rates of solid/fluid reaction, comminution of solid starting materials introduces yet another potential experimental complexity: namely, that the particular steady states achieved during experimentation may depend on the degree of comminution (e.g., see Myers et al., 1984a, Figure 6-4). The only way to eliminate this uncertainty is to conduct experiments with different grain sizes of solid starting materials.

Reaction rates in a system of a given bulk composition are also influenced by the kinds of solid phases that are present. For example, it is generally observed that amorphous solid phases (glasses or gels) are more reactive than crystalline phases. Also, some crystalline phases are more reactive than others.

In summary, it is evident from foregoing discussion that the following factors influence the numbers and kinds of steady states that are achieved and detected in barrier materials + groundwater experiments: (1) sampling protocol, (2) the accuracy and precision of the solubility/concentation data, (3) duration of experimentation, (4) the physical characteristics of the solid starting materials, (5) the degree of crystallinity of the solids in the starting materials, and (6) the kinds of solid phases that are present in the solid starting materials.

Finally, it should be borne in mind that, regardless of the duration of a barrier materials + groundwater experiment, the solid reaction products invariably contain one or more metastable solid phases. Thus, at the conclusion of experimentation, it is usually observed that radionuclides and/or radionuclide-analog elements are either sorbed onto — or incorporated into — a mixture of stable and metastable solid phases. Significantly, these assemblages of solid phases typically do not include many of the radionuclide-bearing and/or radionuclide-analog-element-bearing crystalline phases that geochemical computer codes predict to be stable. The usual explanation for this discrepancy is that stable crystalline phases that incorporate radionuclides and radionuclide-analog elements into their structures are slow to crystallize in hydrothermal experiments.

5.3 DIFFERENCES BETWEEN THE SOLUBILITIES/CONCENTRATIONS LISTED BY MYERS ET AL. (1984a) AND CORRESPONDING VALUES DEVELOPED BY THE AUTHOR

Examining the experimentally-based solubility/concentration data listed in Tables 2-6, it is evident that — with a few minor exceptions — there is generally good numerical agreement between the data listed by Myers et al. (1984a) and corresponding figures developed by the author. However, it is also evident that there are numerous instances in which Myers et al. and the author disagree that a particular solubility/concentration measured at or near the conclusion of an experiment in fact represents a steady-state concentration. Such determinations depend on individual judgments concerning: (1) changes in solubility/concentration with time, and (2) the accuracy and precision of the solubility/concentration data. These judgments can, of course, be highly subjective. But that is precisely the point. The author's principal purpose in reinterpreting some of the key experimental data listed by Myers et al. (1984a) is to show that human judgment can play an important role in identifying steady-state conditions.

5.4 CALCULATED SOLUBILITIES FOR RADIONUCLIDE-ANALOG ELEMENTS AT 25°C

DOE-Hanford data on the solubilities/concentrations of radionuclide-analog elements at 25°C are described by Early et al. (1982) and Early et al. (1984). Significantly, the latter investigators present both calculated solubilities and a limited quantity of corresponding experimental data (Early et al., 1984, Table II) (See Table 1). Examining these data, it is evident that most of the calculated

solubilities are much lower than the experimentally measured solubilities/concentrations. (See also Table 8-2 in Myers et al., 1984a.)

In attempting to understand why most of the calculated solubilities listed in Table 1 are significantly lower than corresponding experimentally measured solubilities/concentrations, it should be kept in mind that the calculated solubilities are really not directly comparable to the experimentally measured solubilities/concentrations. This is so principally because the calculated solubilities are based on the unrealistic assumption that it is possible to achieve essentially complete (stable) thermodynamic equilibrium between groundwater and coexisting solid phases. This assumption is unrealistic because it ignores the potentially important effects of: (1) the presence of significant quantities of colloids and/or particulates, and (2) sluggish solid/fluid reaction kinetics (i.e., the crystallization and/or persistence of metastable solid phases).

In view of the failure to account for the effects of solid/fluid reaction kinetics, it is not surprising that the calculations performed by Early et al. (1984) predict an assemblage of solids + groundwater that has never been observed to form in <u>any</u> barrier materials + groundwater experiment (including experiments performed at temperatures as high as 300°C). This fact underscores a point made previously: namely, that many of the solids which geochemical computer codes indicate should be stable are, in fact, absent in the reaction products of barrier materials + groundwater experiments. In this regard, it

should be recognized that discord between predicted and observed reaction products does not automatically preclude the use of computer codes to analyze the data obtained from barrier materials + groundwater experiments. This is so because current geochemical computer codes are capable of modeling metastable equilibria. Unfortunately, however, the available thermodynamic data for many key solid phases (e.g., waste glass, basalt glass, and many radionuclide-bearing crystalline phases) are either inaccurate, incomplete, or totally lacking. Therefore, at present, it is very difficult to employ geochemical computer codes to properly model metastable equilibria in barrier materials + groundwater systems.

It is evident from the discussion above that many of the discrepancies between calculated solubilities and measured solubilities/concentrations can be attributed to sluggish solid/fluid reaction kinetics in barrier materials + groundwater experiments. However, there is yet another potential difficulty in employing computer codes to calculate the solubilities of radionuclides and/or radionuclide-analog elements. This difficulty is that the assemblage of solid phases that a geochemical code predicts to be stable may, in fact, not be the most stable assemblage of solid phases for the particular set of geochemical conditions (bulk composition, pressure, temperature) under consideration.* It is a well established fact that the phase relations of multicomponent systems can be very sensitive to bulk composition and temperature. Therefore, multicomponent phase relations predicted by computer codes should be considered hypothetical until unambiguously

validated by careful experimentation.

For the reasons cited above, there is little hope that, in the near future, geochemical computer codes will provide calculated solubilities that are accordant with experimentally measured solubilities/concentrations. Consequently, in the meantime, we are left to rely on the empirical rule of thumb that, due to the fact that the reaction products of barrier materials + groundwater experiments typically contain one or more metastable solid phases, measured solubilities/concentrations of nuclides will generally be higher than corresponding solubilities predicted by geochemical computer codes.

---

*This problem is of potential consequence in predicting the solubilities/concentrations of nuclides in natural environments or laboratory experiments where it is at least possible to achieve complete thermodynamic equilibrium; for instance, in favorable local regions of natural rock/groundwater systems, and in hydrothermal experiments performed at elevated temperatures (say, at temperatures above approximately 250°C).

6. MAJOR CONCLUSIONS

The author has reached the following major conclusions concerning DOE-Hanford information on the solubilities/concentrations of radionuclide-analog elements in simulated waste form ± Umtanum basalt + Grande Ronde groundwater systems.

1. DOE-Hanford experimental data on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems at 90 to 300°C are sparse, and most of the available data have been obtained under experimental conditions which do not adequately simulate the geochemical conditions that are expected to prevail near waste packages in an NWRB after the containment period.

DOE-Hanford staff members and contractors have performed only a small number of experiments on the solubilities/concentrations of radionuclide-analog elements, and all of the systems investigated to date are simulated waste form ± Umtanum basalt + Grande Ronde groundwater systems. Therefore, several promising research areas remain to be explored. For example, the effects of simulated-waste-form composition on the solubilities/concentrations of radionuclide-analog elements are only partly documented. Until these effects are more fully elucidated, it will remain uncertain whether the solubilities/concentrations of some radionuclide-analog elements can be affected significantly by relatively small changes in the chemical composition of the simulated waste form.

Another problem with DOE-Hanford experimental data on the solubilities/concentrations of radionuclide-analog elements is that the data acquired to date have been obtained under experimental conditions which do not

adequately simulate the geochemical conditions that are expected to prevail near waste packages in an NWRB after the containment period. For example, DOE-Hanford use of freshly crushed basalt as a solid starting material in simulated waste form + basalt + groundwater experiments is inappropriate because the crushed basalt in the packing material of waste packages in an NWRB would probably be partly to mostly altered to secondary minerals by the end of the containment period. Also, the geochemical effects of other waste package materials — e.g., canister metal and cladding — have not been investigated.

Finally, another difficulty for DOE-Hanford is that the results of hydrothermal experiments may be influenced by the physical states of the solid starting materials (e.g., the grain size of basalt starting materials).

2. There is a paucity of experimental data on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems at "low" temperatures (25 to 90°C).

Experimental data on the solubilities/concentrations of radionuclide-analog elements at low temperatures (25 to 90°C) are needed to determine the extent to which "solubility" would decrease the mobilities of radionuclides in the far field of an NWRB at the Hanford Site. Experimental data are especially needed for those radionuclide-analog elements which: (1) have comparatively high "solubilities" in Grande Ronde groundwaters at 25 to 90°C, and/or (2) are not readily sorbed by the primary and secondary minerals in Hanford-Site basalts and interbed rocks.

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

DOE-Hanford 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/concentration data obtained by DOE-Hanford and its contractors (Myers et al., 1984a).

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. However, the amounts of dissolved radionuclides in such a system 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 statement 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 sorbed trace components.

Experimental evidence that supports these assertions includes the data that DOE-Hanford has obtained on the concentration-vs-time behavior of cesium in an experiment performed on the system simulated spent fuel + Umtanum basalt + GR-3 groundwater at 300°C. During this experiment — run BSF-3 described by Myers et al. (1984a, Figure A-8) — the concentration of cesium, initially ~3 mg/L, increased sharply to ~48 mg/L after 1 h, remained nearly constant through 3 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 to the presence of variable quantities of cesium-bearing particulates and/or colloids in the synthetic groundwaters, it may be concluded that, after initially reaching a comparatively high concentration due to relatively rapid dissolution of the waste form, it is not <u>necessarily</u> true that the "solubility" of a dissolved radionuclide will thereafter always either remain constant or continuously decrease with increasing time.

4. <u>DOE-Hanford staff members and contractors have neglected to calculate or estimate the precision of their solubility/concentration data</u>.

DOE-Hanford reports that contain data on the solubilities/concentrations of radionuclides and radionuclide-analog elements (e.g., Apted and Myers, 1982; Myers et al., 1984a) do not present calculated or estimated limits of error for the data. This omission is unfortunate because, in certain circumstances, the significance of solubility/concentration data can be difficult to assess when the precision of the data is unknown.

5. 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.

A "fate of radionuclides" approach to barrier materials + groundwater experimentation (Apted, 1982) is a useful strategy for obtaining data that are needed for 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 (or radionuclide-analog elements) 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 sorbed radionuclides. The task of identifying these solids is made difficult by the fact that, in most experiments, there are only small amounts of radionuclides present in the solid reaction products. Thus, it is not surprising that DOE-Hanford has experienced some difficulty in identifying and characterizing the radionuclide-bearing and radionuclide-analog-element-bearing solid phases that are present in experimental run products.

6. It is possible to obtain "reversals" of nuclide solubilities/concentrations measured during experiments with Dickson-type apparatus.

DOE-Hanford staff members and contractors should be aware that it is possible to "reverse" nuclide solubilities/concentrations measured during experiments with Dickson-type apparatus. 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 small quantity of radionuclide-rich fluid is injected into the gold bag in the pressure vessel. This injection should cause the groundwater in the vessel to become supersaturated with radionuclides. More specifically, if, prior to the injection event, the concentrations of groundwater-borne radionuclides represent steady-state concentrations, then, after the injection event, 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 bag in the pressure vessel, thereby diluting the nominally radionuclide-saturated synthetic groundwater in the vessel. This mixing should induce dissolution of "radionuclide-rich" solid phases (if they are present), and/or initiate "release" of sorbed radionuclides to the groundwater, thereby causing the concentrations of radionuclides to increase toward their original values.

Following the two procedures outlined above for reversing (bracketing) measured concentrations of radionuclides, it would be possible to establish ranges of radionuclide concentration which encompass the "true" steady-state solubilities/concentrations of the radionuclides.

7. REFERENCES

Altenhofen, M. K., Waste-Package Heat-Transfer Analysis: Model Development and Temperature Estimates for Waste Packages in a Repository Located in Basalt, RHO-BWI-ST-18, Rockwell Hanford Operations, Richland, Washington, 1981.

Apted, M. J., Overview of Hydrothermal Testing of Waste Package Barrier Materials at the Basalt Waste Isolation Project, PNL-4382, Pacific Northwest Laboratory, Richland, Washington, 1982.

Apted, M. J., and J. Myers, Comparison of the Hydrothermal Stability of Simulated Spent Fuel and Borosilicate Glass in a Basaltic Environment, RHO-BW-ST-38 P, Rockwell Hanford Operations, Richland, Washington, 1982.

Benson, L. V. and L. S. Teague, A Tabulation of Thermodynamic Data for Chemical Reactions Involving 58 Elements Common to Radioactive Waste Package Systems, Topical Report No. 4 for Rockwell Hanford Operations, LBL-11448, Lawrence Berkeley Laboratory, University of California, Berkeley, California, 1980.

Bradley, D. J., C. O. Harvey, and R. P. Turcotte, Leaching of Actinides and Technetium from Simulated High-Level Waste Glass, PNL-3152, Pacific Northwest Laboratory, Richland, Washington, 1979.

DOE, Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3, 3 Volumes, Rockwell Hanford Operations for the U.S. Department of Energy, Washington, D.C., 1982.

DOE, Environmental Assessment, Reference Repository Location, Hanford Site, Washington, DOE/RW-0070, 3 Volumes, Washington, D.C., 1986.

Early, T. O., G. K. Jacobs, D. R. Drewes, and R. C. Routson, Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt: Estimated Solubilities for Selected Elements, RHO-BW-ST-39 P, Rockwell Hanford Operations, Richland, Washington, 1982.

Early, T. O., G. K. Jacobs, and D. R. Drewes, "Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt," Am. Chem. Soc. Symp. Ser. 246, p. 147-166, 1984.

EPA, Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes, 40 CFR Part 191, U.S. Environmental Protection Agency, Washington, D.C., Federal Register, Vol. 50, No. 182, p. 38066, 1985.

Gephart, R. E., R. C. Arnett, R. G. Baca, L. S. Leonhart, and F. A. Spane, Jr., Hydrologic Studies Within the Columbia Plateau, Washington: An Integration of Current Knowledge, RHO-BWI-ST-5, Rockwell Hanford Operations, Richland, Washington, 1979.

Grandstaff, D. E., G. L. McKeon, E. L. Moore, and G. C. Ulmer, "Reactions in the System Basalt/Simulated Spent Fuel/Water," in G. L. McVay, ed. Scientific Basis for Nuclear Waste Management VII, Materials Research Society Symposia Proceedings, 26, p. 137-145, 1984.

Gray, W. J., "Gamma Radiolysis Effects on Grande Ronde Basalt Groundwaters," in G. L. McVay, ed. Scientific Basis for Nuclear Waste Management VII, Materials Research Society Symposia Proceedings, 26, p. 147-152, 1984.

Holloway, J. R., D. M. Jenkins, J. F. Kacoyannakis, and M. J. Apted, The Geochemical Behavior of Supercalcine Waste Form: Its Stability in a Basalt Environment, RHO-BWI-C-105, Rockwell Hanford Operations, Richland, Washington, 1981.

Jones, T. E., Reference Material Chemistry, Synthetic Groundwater Formulation, RHO-BW-ST-37 P, Rockwell Hanford Operations, Richland, Washington, 1982.

Kelmers, A. D., J. H. Kessler, F. G. Seeley, W. D. Arnold, R. E. Meyer, F. J. Smith, N. H. Cutshall, G. K. Jacobs, S. Y. Lee, and S. K. Whatley, Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Annual Progress Report for October 1983 - September 1984, NUREG/CR-3851, ORNL/TM-9191, Vol. 4, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1985.

Krupka, K. M., E. A. Jenne, and W. J. Deutsch, Validation of the WATEQ4 Geochemical Model for Uranium, PNL-4333, Pacific Northwest Laboratory, Richland, Washington, 1983.

Langmuir, D., "Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits," Geochimica et Cosmochimica Acta, 42, 1982.

Lemire, R. J., and P. R. Tremaine, "Uranium and Plutonium Equilibria in Aqueous Solutions to 200°C," J. Chem. and Engr. Data, 25, 1982.

Long, P. E., and WCC (Woodward-Clyde Consultants), Repository Horizon Identification Report, SD-BWI-TV-001 DRAFT, Vols. 1 and 2, for Rockwell Hanford Operations, Richland, Washington, 1984.

McVay, G. L., and C. O. Buckwalter, "Effect of Iron on Waste-Glass Leaching," J. American Ceramic Soc., 66, p. 170-74, 1983.

Means, J. L., The Organic Geochemistry of Deep Groundwaters, ONWI-268, Battelle Columbus Laboratories, Columbus, Ohio, 1982.

Myers, C. W., S. M. Price, J. A. Caggiano, M. P. Cochran, W. J. Czimer, N. J. Davidson, R. C. Edwards, K. R. Fecht, G. E. Holmes, M. G. Jones, J. R. Kunk, R. D. Landon, R. K. Ledgerwood, J. T. Lillie, P. E. Long, T. H. Mitchell, E. H. Price, S. P. Reidel, and A. M. Tallman, Geologic Studies of the Columbia Plateau: A Status Report, RHO-BWI-ST-4, Rockwell Hanford Operations, Richland, Washington, 1979.

Myers, C. W., and S. M. Price, eds., Subsurface Geology of the Cold Creek Syncline, RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington, 1981.

Myers, J., 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, Rockwell Hanford Operations, Richland, Washington, 1983.

Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Rockwell Hanford Operations, Richland, Washington, 1984.

Myers, J., G. C. Ulmer, D. E. Grandstaff, R. Brozdowski, M. J. Danielson, and O. H. Koski, "Developments in the Monitoring and Control of Eh and pH Conditions in Hydrothermal Experiments," Geochemical Behavior of Disposed Radioactive Waste, Am. Chem. Soc. Symp. Ser. 246, p. 197-216, 1984.

Nair, G. M., K. Chandler, and J. K. Joshi, "Hydroloysis Constants of Plutonium(III) and Americium(III)," Radiochimica Acta, 30, p. 37-40, 1982.

NRC, Disposal of High-Level Radioactive Wastes in Geologic Repositories, Technical Criteria, 10 CFR Part 60, Federal Register, Vol. 48, No. 120, p. 28194, 1983.

Olofsson, U., and B. Allard, Complexes of Actinides with Naturally Occurring Organic Substances — Literature Survey, KBS Technical Report 8309, Stockholm, Sweden, 1983.

Phillips, S. L., "Hydroloysis and Formation Constants at 25°C," LBL-14313, Lawrence Berkeley Laboratory, University of California, Berkeley, California, 1982.

Rai, D., and R. J. Serne, "Solid Phases and Solution Species of Different Elements in Geologic Environments," PNL-2651, Pacific Northwest Laboratory, Richland, Washington, 1978.

Rai, D., R. J. Strickert, and D. A. Moore, "Am(III) Hydrolysis Constants and Solubility of Am(III) Hydoxide," PNL-SA-10635, Pacific Northwest Laboratory, Richland, Washington, 1982.

Smith, M. J., BWIP Data Package for Reference Chemistry of and Procedures for Preparation of Synthetic Grande Ronde Basalt and Mabton Interbed Groundwaters, RSD-BWI-DP-007, Rockwell Hanford Operations, Richland, Washington, 1981.

Stumm W., and J. J. Morgan, Aquatic Chemistry, John Wiley & Sons, New York, 2nd ed., 1981.

Thomas, L. E., B. Mastel, and E. D. Jenson, Examination of Solids from 200°C Hydrothermal Tests with Spent Fuel, SD-BWI-TI-283, Rockwell Hanford Operations, Richland, Washington, 1985.

Westinghouse-AESD, Waste Package Concepts for Use in the Conceptual Design of the Nuclear Waste Repository in Basalt, RHO-BW-CR-136 P, Rockwell Hanford Operations, Richland, Washington, 1982.

Wood, M. I., G. D. Aden, and D. L. Lane, Evaluation of Sodium Bentonite and Crushed Basalt as Waste Package Backfill Materials, RHO-BW-ST-21 P, Rockwell Hanford Operations, Richland, Washington, 1982.

Wood, M. I., J. F. Relyea, J. Myers, and M. J. Apted, The Near-Field Waste Package Environment in Basalt and Its Effect on Waste Form Releases, RHO-BW-SA-331 P, Rockwell Hanford Operations, Richland, Washington, 1983.

Woodley, R. E., C. N. Wilson, and R. L. Hervig, The Chemical and Physical Characteristics of Spent-Light Water Reactor Fuel and a Method for Simulation of a Non-Radioactive Analog, RHO-BWI-C-114, Rockwell Hanford Operations, Richland, Washington, 1981.

APPENDIX A

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

This appendix contains Tables A.1-A.5, which list the chemical compositions of the solid and fluid starting materials that DOE-Hanford staff members and contractors have used in "high-temperature" (90 to 300°C) hydrothermal experiments on the systems: simulated waste form ± Umtanum basalt + Grande Ronde groundwater.

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_2O_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		

[a]Composition from Woodley et al. (1981).

Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 3-7, Rockwell Hanford Operations, Richland, Washington, 1984.

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

Component	Amount (Wt %)	Component	Amount (Wt %)
SiO_2	39.80	La_2O_3	0.56
Na_2O	12.80	PdO	0.56
Fe_2O_3	10.34	P_2O_5	0.51
B_2O_3	9.47	Cr_2O_3	0.44
ZnO	4.97	SrO	0.40
Nd_2O_3	4.67	Sm_2O_3	0.35
TiO_2	2.97	TeO_2	0.28
MoO_3	2.42	Y_2O_3	0.23
CaO	2.00	NiO	0.21
ZrO_3	1.88	Rh_2O	0.18
CeO_2	1.26	Rb_2O	0.18
RuO_2	1.13	Eu_2O_3	0.08
Cs_2O	1.09	Gd_2O_3	0.05
BaO	0.59	CdO	0.04
Pr_6O_{11}	0.56	Ag_2O	0.03

[a]Pacific Northwest Laboratory (PNL) 76-68 Composition (McVay, 1983).
Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 3-4, Rockwell Hanford Operations, Richland, Washington, 1984.

Table A.3. Chemical composition of simulated DHLW borosilicate glass[a]

Component	Wt %	Component	Wt %
SiO_2	41.83	Fe_2O_3	13.65
Na_2O	12.43	MnO_2	3.93
B_2O_3	10.32	Zeolite[b]	2.94
TiO_2	0.70	Al_2O_3	2.74
Li_2O	4.00	NiO	1.53
MgO	1.40	Na_2CO_3	1.18
ZrO_2	0.35	CaO	1.01
La_2O_3	0.35	Coal	0.66
		Na_2SO_4	0.17
		$CsNO_3$	0.15
		$Sr(NO_3)_2$	0.15

[a]Savannah River Laboratory Type 131/TDS Waste Glass Composition.
[b]Linde AW-500 Zeolite (Calcium-Aluminum-Silicate).
Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 3-6, Rockwell Hanford Operations, Richland, Washington, 1984.

Table A.4. 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_2O_3	13.71	0.27
Fe_2O_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_2O	2.95	0.29
K_2O	1.63	0.06
P_2O_5	0.35	0.02
Modal mineralogy		
Plagioclase (An_{40})		28.7
Pyroxene		17.1
Mesostasis		47.7
Titaniferous magnetite		5.12
Chlorophaeite		1.65
		100.27

Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 3-1, Rockwell Hanford Operations, Richland, Washington, 1984.

Table A.5. Chemical compositions of synthetic groundwaters used in high-temperature hydrothermal experiments

Dissolved constituent	Concentrations in mg/L	
	GR-A[a]	GR-3[b]
Na^+	250	358
K^+	1.9	3.4
Ca^{2+}	1.3	2.8
Mg^{2+}	0.04	0.032
Cl^-	148	312
CO_3^{2-}	30	12.9
HCO_3^-	36	42.9
F^-	37	33.4
SO_4^{2-}	108	173
SiO_2	86.6	76.2
pH	10.2	9.9

[a]Data from Holloway (1981).
[b]Data from Smith (1981).
Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 3-2, Rockwell Hanford Operations, Richland, Washington, 1984.

APPENDIX B

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

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

Summaries and interpretations of the results of DOE-Hanford hydrothermal experiments are presented below for each individual 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 figures listed or cited are based on data presented by Apted and Myers (1982) and Myers et al. (1984a). These investigators do not list statistically determined or empirically estimated uncertainties for their data and, therefore, no attempt has been made here to account for the potential effects of such uncertainties.

In describing changes in groundwater composition during "typical" DOE-Hanford experiments, the author has attempted to correctly identify groundwater solute elements/species that exhibited steady-state (constant concentration-vs-time) behavior either briefly or continuously during each experiment. For comparison, this appendix also includes

Tables B.1-B-5 which present conclusions drawn by Myers et al. (1984a) concerning whether or not particular radionuclide-analog elements exhibited steady-state behavior during the selected experiments. Comparing the interpretations given in this report with those presented by Myers et al., it is evident that there are significant differences of opinion in some instances. These discrepancies are largely attributable to scatter in the concentration-vs-time data. Finally, the summaries of selected DOE-Hanford experimental results presented below include listings of the secondary minerals/solid phases that formed during each experiment. The source of this information is Table 6-2 in Myers et al. (1984a).

B.1 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED SPENT FUEL + GR-3 GROUNDWATER

Experiments on this system were performed by DOE-Hanford staff members and are described by Apted and Myers (1982) and Myers et al. (1984a).

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.5) 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 the Concentrations of Aqueous Sodium, Silicon, and Sulfate

Measured changes in the concentrations of sodium, silicon, and sulfate in groundwaters at 100, 200, and 300°C are documented below [see Apted and Myers (1982, Table 11) and Myers et al. (1984a, Figures A-2, A-3, and A-4)].

B.1.3.1 100°C (run D6-8)

The concentration of sodium, 420 mg/L after 1 h, decreased slightly throughout the experiment, reaching 378 mg/L after 714 h. The concentration of silicon, ~34 mg/L after 1 h, remained essentially constant for 161 h, and then decreased slightly to ~27 mg/L after 714 h. The concentration of sulfate, 34 mg/L after 1 h, 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 and Myers, 1982), increased to 380 mg/L after 1 h, and thereafter remained essentially constant. The concentration of silicon, initially 33 mg/L (Apted and Myers, 1982), increased to ~59 mg/L after 48 h, and thereafter slowly decreased, reaching a concentration of 51 mg/L after 532 h. The concentration of sulfate, 30 mg/L after 1 h, decreased to an apparent steady-state concentration of ~18 mg/L after 20 h.

B.1.3.3 300°C (run D5-1)

The concentration of sodium, initially 381 mg/L (Myers et al., 1984a), remained nearly constant during the experiment. The concentration of silicon, initially ~32 mg/L (Myers et al., 1984a), 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 sulfate, initially 35 mg/L (Myers et al., 1984a), 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 Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclide-analog elements in groundwaters at 100, 200, and 300°C are documented below [see pertinent run tables in Myers et al. (1984a, Figures A-2, A-3, and A-4), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1984a, Table 8-2), which are summarized in Table B.1.]

B.1.5.1 100°C (run D6-8)

The concentration of molybdenum 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 rose to ~0.9 mg/L after 1 h, and then decreased to an apparent steady-state concentration of ~0.3 mg/L after 161 h. The concentration of strontium, ~0.16 mg/L after 1 h, decreased erratically 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 and Myers, 1982), increased sharply to a concentration of ~60 mg/L after 1 h, and then rose to an apparent steady-state concentration of ~68 mg/L after 20 h. The concentration of barium, initially 0.001 mg/L (Apted and Myers, 1982), 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 332 h. The concentration of strontium, 0.019 mg/L after 1 h (Myers et al., 1984a), decreased erratically to a concentration of 0.011 mg/L after 532 h.

B.1.5.3 300°C (run D5-1)

The concentration of molybdenum, initially ~2 mg/L (Myers et al., 1984a), 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 2.29 mg/L (Myers et al., 1984a), decreased sharply to an apparent steady-state concentration of ~0.09 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 et al., 1984a), decreased to an apparent steady-state concentration of ~0.008 mg/L after 20 h.

B.2 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED SPENT FUEL + UMTANUM BASALT + GR-3 GROUNDWATER

Experiments on this system were performed by geochemists at Temple University and are described by Apted and Myers (1982) and Myers et al. (1984a).

B.2.1 Starting Materials

Starting materials were simulated spent fuel (Appendix A, Table A.1), Umtanum basalt (Appendix A, Table A.4), and GR-3 synthetic groundwater (Appendix A, Table A.5) 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 the concentrations of Aqueous Sodium, Silicon, and Sulfate

Measured changes in the concentrations of sodium, silicon, and sulfate in groundwaters at 100, 200, and 300°C are documented below [see Myers et al. (1984a, Figures 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 essentially 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 nearly constant. The concentration of sulfate, 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 ~120 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 ~285 mg/L after just 1 h, but later — between 1197 h and 2014 h — it apparently decreased further from ~300 mg/L to 239 mg/L. The concentration of silicon, initially ~36 mg/L, increased sharply to ~174 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 sulfate, initially 190 mg/L, decreased slightly to an apparent steady-state concentration of 170 mg/L after 20 h, remained nearly constant through 1197 h, and then apparently 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 fairly 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 sulfate, 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, a cesium-bearing phyllosilicate, scapolite, powellite-scheelite, palladium sulfide, and heulandite.

The silica formed in run BSF-3 exhibited poorly developed crystal faces. 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 Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclide-analog elements in groundwaters at 100, 200, and 300°C are documented below [see pertinent run tables in Myers et al. (1984a, Figures A-5, A-6, and A-8), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1984a, Table 8-2), which are summarized in Table B.2].

B.2.5.1 100°C (run BSF-4)

The concentration of molybdenum rose rapidly to 46.6 mg/L after 1 h, remained essentially constant through 52 h, and then gradually increased to an erratic 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 ~2 mg/L 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 increased to an apparent inventory-limited concentration of ~11 mg/L after just 1 h. The concentration of uranium rose rapidly to 1.18 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 nearly constant through 44 h, and then decreased gradually to a new apparent steady-state concentration of ~0.3 mg/L (the initial concentration) after 357 h. The concentration of cesium increased sharply to 47.6 mg/L after 1 h, remained nearly 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 are being disregarded by DOE-Hanford. The concentration of uranium 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 nearly 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 nearly 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 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 + GR-A 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. (1984a).

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.5) 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 3900 h, 3048 h, and 1008 h, respectively.

B.3.3 Changes in the Concentrations of Aqueous Sodium, Silicon, and Boron

Measured changes in the concentrations of sodium, silicon, and boron in groundwaters at 100, 200, and 300°C are documented below [see Myers et al. (1984a, Figures A-10, A-12, and A-14)].

B.3.3.1 100°C (run GLSW 3-1)

The concentration of sodium rose steadily during the experiment, reaching a concentration of 2054 mg/L after 2584 h. The concentration of silicon 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 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 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 rose sharply to 640 mg/L after 3 h, then increased steadily to 1330 mg/L after 1533 h, and thereafter decreased sharply to 805 mg/L after 3020 h. The concentration of boron 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 9 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 16 h, and thereafter varied erratically between 1040 and 1280 mg/L. 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 occurred 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): a 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 Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclide-analog elements in groundwaters at 100, 200, and 300°C are documented below [see pertinent run tables in Myers et al. (1984a, Figures A-10, A-12, and A-14), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1984a, Table 8-2), which are summarized in Table B-3].

B.3.5.1 100°C (run GLSW 3-1)

The concentration of molybdenum 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 increased fairly steadily to 1.53 mg/L after 836 h, remained essentially constant through 1240 h, and then decreased to 1.08 mg/L after 2584 h. The concentration of strontium rose gradually 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 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 increased sharply to 0.45 mg/L after 12 h, and thereafter decreased to an apparent (and erratic) steady-state concentration of ~0.04 mg/L after 54 h. The concentration of strontium apparently reached a steady-state concentration of ~0.01 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 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 (and erratically) to 0.89 mg/L after 16 h, and thereafter declined sharply to an apparent steady-state concentration of ~0.12 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 + UMTANUM BASALT + GR-A 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. (1984a).

B.4.1 Starting Materials

Starting materials were simulated CHLW borosilicate glass (Appendix A, Table A.2), Umtanum basalt (Appendix A, Table A.4), and GR-A synthetic groundwater (Appendix A, Table A.5) 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 5278 h, 2907 h, and 933 h, respectively.

B.4.3 Changes in the Concentrations of Aqueous Sodium, Silicon, and Boron

Measured changes in the concentrations of sodium, silicon, and boron in groundwaters at 100, 200, and 300°C are documented below [see Myers et al. (1984a, Figures A-15, A-16, and A-17)].

B.4.3.1 100°C (run BGLW 3-1)

The concentration of sodium rose fairly steadily to an apparent steady-state concentration of ~700 mg/L after 792 h. The concentration of silicon 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 rose erratically to 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 fairly steadily during the experiment, reaching a concentration of ~2000 mg/L after 2906 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 steadily during the experiment, reaching 920 mg/L after 2906 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, remained essentially constant through 258 h, and then rose steadily to 1640 mg/L after 1640 h.

B.4.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains. Borosilicate glass fragments occurred as rounded grains and, in 300°C experiments, were 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 Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclide-analog elements in groundwaters at 100, 200, and 300°C are documented below [see pertinent run tables in Myers et al. (1984a, Figures A-15, A-16, and A-17), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1984a, Table 8-2), which are summarized in Table B.4].

B.4.5.1 100°C (run BGLW 3-1)

The concentration of molybdenum rose steadily to ~54 mg/L after 405 h, and thereafter rose erratically to a concentration of ~69 mg/L after 5086 h. The concentration of barium rose fairly 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 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 fairly 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 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 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, decreased to an apparent steady-state concentration of ~0.01 mg/L after 8 h, remained fairly constant through 478 h, and then increased to 0.02 mg/L after 932 h.

B.5 RESULTS OF EXPERIMENTS ON THE SYSTEM: SIMULATED DHLW BOROSILICATE GLASS + UMTANUM BASALT + GR-3 GROUNDWATER

Experiments on this system were performed by DOE-Hanford staff members and are described by Myers et al. (1984a).

B.5.1 Starting Materials

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

B.5.2 Experimental Conditions

Experiments were performed at 10 MPa, 90°C (run D7-1) and 150°C (run D8-1) for 3332 h and 2660 h, respectively.

B.5.3 Changes in the Concentrations of Aqueous Sodium, Silicon, and Boron

Measured changes in the concentrations of sodium, silicon, and boron in groundwaters at 90 and 150°C are documented below [see Myers et al. (1984a, Figures A-21 and A-23)].

B.5.3.1 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.5.3.2 150°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 ~402 mg/L after 144 h, and thereafter increased steadily to a concentration of ~1093 mg/L after 2202 h. The concentration of boron, initially 0 mg/L, increased continuously during the experiment, reaching a maximum concentration of ~681 mg/L after 2202 h.

B.5.4 Solid Experimental Products

Solid experimental products were discrete and unconsolidated crystals or grains. Borosilicate glass fragments occurred 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.5.5 Concentrations of Radionuclide-Analog Elements

Measured changes in the concentrations of radionuclide-analog elements in groundwaters at 90 and 150°C are documented below [see pertinent run tables in Myers et al. (1984a, Figures A-21 and A-23), and compare the conclusions presented here with corresponding conclusions drawn by Myers et al. (1984a, Table 8-2), which are summarized in Table B.5].

B.5.5.1 90°C (run D7-1)

The concentration of barium, initially 0 mg/L, increased to ~0.07 mg/L after 812 h, and then declined to 0.037 mg/L after 2228 h. The concentration of strontium, initially 0 mg/L, reached an apparent steady-state concentration of ~0.005 mg/L after 331 h.

B.5.5.2 150°C (run D8-1)

The concentration of barium, initially 0 mg/L, rose to 0.034 mg/L after 144 h, declined to 0.019 mg/L after 480 h, and then decreased further to an apparent steady-state concentration of 0.012 mg/L after 888 h. 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 (see Appendix A, Table A.1).
W = GR-3 synthetic groundwater (see Appendix A, Table A.5).
NA = Not analyzed.
NI = Not in inventory.
[a]Non-steady-state.
Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt Under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 8-2, Rockwell Hanford Operations, Richland, Washington, 1984.

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

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 (see Appendix A, Table A.1).
B = Umtanum basalt (see Appendix A, Table A.4).
W = GR-3 synthetic groundwater (see Appendix A, Table A.5).
NA = Not analyzed.
NI = Not in inventory.
[a]Inventory limited.
[b]Non-steady-state.

Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 8-2, Rockwell Hanford Operations, Richland, Washington, 1984.

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 (see Appendix A, Table A.2).
W = GR-A synthetic groundwater (see Appendix A, Table A.5).
NA = Not analyzed.
NI = Not in inventory.
[a]Inventory limited.

Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 8-2, Rockwell Hanford Operations, Richland, Washington, 1984.

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

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 (see Appendix A, Table A.2).
B = Umtanum basalt (see Appendix A, Table A.4).
W = GR-A synthetic groundwater (see Appendix A, Table A.5).
NA = Not analyzed.
NI = Not in inventory.
[a]Inventory limited.

Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 8-2, Rockwell Hanford Operations, Richland, Washington, 1984.

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

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 (see Appendix A, Table A.3).
B = Umtanum basalt (see Appendix A, Table A.4).
W = GR-3 synthetic groundwater (see Appendix A, Table A.5).
NA = Not analyzed.
NI = Not in inventory.

Source: Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59 P, Table 8-2, Rockwell Hanford Operations, Richland, Washington, 1984.