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# Review and Assessment of Radionuclide Sorption Information for the Basalt Waste Isolation Project Site

(1979 Through May 1983)

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Prepared by A. D. Kelmers

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Prepared for  
U.S. Nuclear Regulatory  
Commission

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Chemical Technology Division

REVIEW AND ASSESSMENT OF RADIONUCLIDE SORPTION INFORMATION FOR THE  
BASALT WASTE ISOLATION PROJECT SITE (1979 THROUGH MAY, 1983)

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## ABSTRACT

This document presents a scientific review and technological assessment of the radionuclide sorption information reported by the Basalt Waste Isolation Project (BWIP) for the candidate high-level waste repository in the Columbia River basalt flows in the Hanford Reservation. Quantified radionuclide sorption data are necessary for repository performance assessment calculations to model expected radioactivity release rates in groundwater-intrusion - groundwater-migration scenarios. Three key BWIP reports were identified which contain most of the sorption information for a number of radionuclides with basalt, secondary minerals, or interbed materials. An extended review of these data is presented in the document. The technological assessment identified potentially significant deficiencies in the radionuclide sorption information published by BWIP that could lead to questionable or nonconservative radioactivity release calculations in site performance assessment modeling. These deficiencies are discussed in the document in detail. Additional information needs were also defined and described.

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REVIEW AND ASSESSMENT OF RADIONUCLIDE SORPTION INFORMATION FOR THE  
BASALT WASTE ISOLATION PROJECT SITE (1979 THROUGH MAY, 1983)

A. D. Kelmers

1. EXECUTIVE SUMMARY OF THE ASSESSMENT

This document presents a scientific review and technological assessment of the radionuclide sorption information for the basalt candidate high-level waste repository developed by the Basalt Waste Isolation Project (BWIP). All relevant BWIP reports available as of May 1983, including the BWIP Site Characterization Report, were reviewed, and information from them was utilized in the preparation of this document. This document was revised in June 1984.

1.1 INFORMATION DEFICIENCIES

The information describing radionuclide sorption behavior (distribution coefficients and sorption isotherm data) seems inadequate for either accurate or conservative performance assessment modeling of radioactivity releases to the accessible environment from emplaced waste for groundwater-intrusion - groundwater-migration scenarios. The following informational deficiencies were identified:

1. None of the sorption information has been obtained under the redox conditions that BWIP expects to exist in either the repository near field (engineered facility) or the far field (site host rocks). Sorption behavior is dependent upon the species in solution, and many of the more important radionuclides may undergo valence changes, and thus changes in speciation, depending on the test redox condition. BWIP expects the far field to always be under strongly reducing conditions and for the near field to return to such conditions after repository closure. Much of the radionuclide sorption data was collected under oxic redox conditions (air present). Such data might be considered as representing a limiting value and could be useful in some cases for conservative modeling of bounding condition situations, but BWIP has not taken such a modeling approach. The remainder of the sorption information was collected in the presence of added hydrazine hydrate to attempt to simulate the expected repository groundwater Eh in the laboratory experiments [Eh is the oxidation/reduction potential in volts (V) relative to a hydrogen electrode]. We have strong reservations relative to the use of hydrazine or any added chemical reagent in laboratory experiments to simulate repository redox conditions (see Sect. 4.3.1). We doubt if data collected in this manner can be proven acceptable for modeling purposes. Thus, no radionuclide sorption information has been collected under redox conditions which are relevant to the repository near field or far field.

2. It was not established that the sorption information was collected under steady-state conditions. BWIP has reported only sorption ratio information developed by batch contact methodology for a number of radionuclides. While BWIP has identified the data as "distribution coefficients", they have not shown that the data were obtained under steady-state conditions and the information can only be treated as sorption ratio values and sorption isotherms. Results of desorption experiments to test for sorption/desorption disequilibrium have not been reported, thus the data available cannot be used to support accurate radionuclide release modeling. The sorption ratio information might be considered as conservative for evaluating limiting conditions (since sorption/desorption disequilibrium always leads to increased retardation factors), but BWIP has not taken such a modeling approach.
3. The effect of possible radionuclide multiple speciation on the sorption information was not evaluated. A number of important radionuclides may exist as more than one solution species in BWIP groundwater due to the existence of multiple valences and/or complexes with groundwater constituents such as carbonate or fluoride. Multiple speciation cannot be detected by the batch contact methodology employed by BWIP; it is usually explored through column chromatographic techniques. The sorption ratios or sorption isotherms developed by batch contacts may be highly nonconservative for performance assessment modeling application since a portion of the radionuclide could move more rapidly than predicted with groundwater.
4. The accuracy and precision of the sorption information was not discussed. Some sorption ratio data were reported as a value plus/minus a standard deviation. In some cases, the standard deviation was nearly as large as the value. In other cases, only a single value was given with no indication of possible errors. The performance assessment modeling activity will likely require some treatment of data precision and accuracy; such treatment seems not to be possible with the published information.
5. There was little correlation between the radionuclide hazards ranking published by BWIP and the amount of sorption information collected for various radionuclides. It is not clear that the BWIP sorption activities have focused adequately on the key radionuclides (i.e., those most likely to contribute to radioactivity releases to the environment).
6. The composition of the intruding groundwater will be altered because of hydrothermal and radiolytic reactions with the engineered facility components. All sorption information was measured using synthetic groundwater prepared to simulate the existing in situ groundwater. No consideration was given to the alteration of groundwater composition



or the effect this could have on the sorption behavior. Thus, application of the information measured by BWIP to predict radionuclide behavior in the altered groundwater present in a repository groundwater-intrusion event seems highly uncertain.

7. The groundwater migration pathway through the complex BWIP site basalt and interbed layers has not been defined, thus it cannot be asserted that sorption information has been collected for all rocks or groundwaters which may be involved in a radioactivity release scenario.
8. The geochemical conditions that will prevail through time in the near field (engineered facility) have not been well established since the waste form and load, as well as the engineered facility components, have not been finalized. Thus, it cannot be asserted that sorption information has been collected under all relevant geochemical conditions applicable to release scenario modeling.

#### 1.2 ADDITIONAL INFORMATION NEEDS

A number of additional information needs were identified which could require consideration in order to develop sufficient radionuclide sorption information for the performance assessment modeling activities. These needs are:

1. The redox condition that may prevail in the near field and far field through repository time seems not to be rigorously established. This, then, makes it difficult to design sorption experiments to be representative of the repository redox conditions. BWIP has calculated a strongly reducing groundwater Eh from knowledge of the secondary minerals present. It has not been established, however, that the important minerals are in good chemical communication with the groundwater and, therefore, the calculated Eh value may not represent actual in situ redox conditions. Also, it seems not to be possible to add any endogenous chemical, such as hydrazine, to attempt to poise the sorption tests at a predetermined Eh value and assert that the information obtained is accurate for performance assessment modeling. A less ambiguous approach to the conduct of sorption experiments could be to allow the rock component to establish a "natural" redox condition in the test. This could require the use of controlled atmosphere chambers to isolate the test components from air. Such an experimental approach may be more easily justifiable as being representative of repository redox conditions.

2. Additional sorption information may be needed at temperatures more representative of the near-field conditions. Due to the waste radioactive decay heat, the near field will experience a thermal maximum of 200 to 300°C. Such higher temperature sorption tests could require use of autoclave apparatus. While such tests may not be easy to conduct, they seem important since the behavior of the radionuclides in the near field controls the radionuclide concentrations in the groundwater which will migrate to the far field. Such information may be needed for the performance assessment effort.
3. The accuracy and precision of the sorption information will almost certainly have to be addressed in discussions of radioactivity release to the environment. The "reasonable assurance" criteria of 10 CFR 60 seem to require an understanding of the possible errors or uncertainty in data such as sorption ratios or sorption isotherms.
4. The groundwater composition used in the sorption experiments will probably have to be more rigorously defined. In any groundwater-intrusion-groundwater-migration event the composition of the intruding and migrating groundwater will be altered through hydrothermal and radiolytic reactions with the engineered facility components. Sorption information for use in performance assessment modeling may have to be measured in this altered groundwater in order for the information to be accepted as being either accurate or conservative modeling approaches.
5. As discussed in Sect. 1.1, it likely will be necessary to develop an understanding of sorption/desorption disequilibrium and multiple-speciation effects on the radionuclide sorption information.
6. A number of the aspects of the BWIP repository are not finalized, including such items as waste form and load, or the release pathway from emplaced waste to the accessible environment. Obviously, various repository options have an impact on the geochemical conditions to be effective through time and, in turn, on the design of sorption experiments to obtain information under these geochemical conditions. The establishment of bounding conditions and measurement of limiting sorption values could be an attractive approach to dealing with these geochemical condition uncertainties.

## 2. INTRODUCTION

The following sections present the purpose and scope of this document and give the key sorption data reports upon which this analysis is based.

### 2.1 PURPOSE

The purpose of this document is to provide a scientific review and technological assessment of the radionuclide sorption information that has been developed for the Basalt Waste Isolation Project (BWIP) candidate high-level waste repository. The BWIP site on the DOE Hanford Reservation is in basalt rock in the Pasco Basin region of the Columbia River basalt flows. The BWIP, managed by Rockwell Hanford Operations, has been developing site-characterization information relative to the selection of a reference repository location and for repository design efforts. An important part of this information development is a modeling activity to predict potential radionuclide release rates from emplaced waste to the accessible environment for defined release scenarios. Quantified data for the geochemical processes and conditions which control or affect radionuclide migration/retardation behavior in the repository are important input parameters for the modeling effort. One major constraint on the rate of radionuclide migration is the sorption process, and BWIP radionuclide release calculations may take credit for favorable (i.e., high) retardation factors for many radionuclides under expected repository geochemical conditions. Therefore, an important aspect of the NRC site-characterization analysis activities must include an assessment of the quality of the BWIP sorption data and an evaluation of uncertainties, as well as the completeness of the information and identification of needed additional data. This report has been prepared as a portion of that NRC assessment effort.

### 2.2 SCOPE

This document includes all references identified as of May 1983 which contain BWIP radionuclide sorption information. Primary emphasis was given to several of the most recent BWIP reports because data in some earlier reports were either summarized and included in these, or were superseded by newer data in the later reports. The reports identified are included in Sect. 7, "REFERENCES."

The report is divided into four general areas. Section 3 contains a collation and summary of radionuclide sorption information. The information has been sorted by categories and is presented in a condensed format. Section 4 contains a technological analysis of the information, including discussions of accuracy and uncertainties, as well as relevance to the BWIP sorption issue (Sect. 4.5). Finally, Sect. 5 identifies additional information needs.

### 2.3 KEY SORPTION DATA REPORTS

The following are the three key primary reports that contain the most recent and extensive tabulations of sorption information for the BWIP site:

1. Basalt Primary Phases (SALTER 1981b),
2. Basalt Secondary Minerals (SALTER 1981a), and
3. Interbed Materials (BARNEY 1982).

The most complete listing of evaluated and recommended "conservative best-estimate" radionuclide sorption distribution coefficient values are contained in the BWIP Site Characterization Report for the Basalt Waste Isolation Project (SCR 1982). Extensive use was made of the information in these key reports during preparation of this document.

### 3. INFORMATION REVIEW

The following sections present a review of radionuclide sorption information available as of May 1983, including a description of the BWIP site, geologic materials, experimental procedures, and results.

#### 3.1 BWIP SITE DESCRIPTION

The basalt flow geology and hydrology in the Hanford Reservation are both monotonous and complex. [The most recent published review of the site geology and geochemistry is included in the Site Characterization Report (SCR 1982).] Flows of basaltic magma have repeatedly erupted over millions of years and covered an extensive area of western Washington, eastern Idaho, northern Nevada, and northern Oregon with multiple layers of basalt. In the Pasco Basin, the basalt depth exceeds 1000 m. Each lava flow formed a discrete horizon in the rock stratigraphy and is characterized by a brecciated flow bottom and flow top which are more permeable and porous than the columnar or entablature basalt. In addition, several periods of extended magmatic inactivity occurred, and a weathered surface developed and accumulation of extraneous (nonbasaltic) materials occurred; these materials were subsequently buried under more basalt flows. These interbed strata have been identified as "interbed" regions, and some are now the location of major fresh water aquifers.

The BWIP reference repository location initially was in a specific Grande Ronde basalt flow (the Umtanum) at 1000-m depth. Recent information indicates that the reference repository level may be moved upwards in the Grande Ronde from the Umtanum to the Cohasset flow, but all published reports identify the Umtanum as the candidate repository level, and that designation will be followed in this document. The Umtanum is one of the many flows that comprise the Grande Ronde basalt sequence, which was deposited approximately 16 million years ago. The hydrologic information at this depth is not complete, but there may be significant quantities of groundwater in the permeable basalt layer flowtops. The reference repository level is hundreds of meters below the interbed aquifers.

The ambient physicochemical parameters in the Umtanum as identified by BWIP (SALTER and JACOBS 1981) are: temperature, 59°C; pressure, 114 bars; groundwater composition,  $\text{Na}^+ \gg \text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+} > \text{Fe}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-} > \text{F}^-$ , and  $\text{SiO}_2$  saturated; pH, 9.6; and, Eh, -0.48 V. With the exception of Eh, these parameters were measured. The low Eh values was inferred from knowledge of the mineral assemblage. Measured groundwater Eh values have ranged from -0.2 V to +0.2 V. The expected basalt major primary mineral phases (SALTER 1981b) are labradorite and augite with lesser amounts of titaniferous magnetite. The major secondary minerals (SALTER 1981a) are expected to be smectite clays, zeolites, and silica phases. A significant portion of the basalt mesostasis is groundmass that exists as a silica-rich glass. The BWIP geochemical conditions will be treated in depth in a parallel review and assessment report currently under preparation.

The probable release pathways for radionuclide migration from the emplaced waste in the reference repository to the accessible environment (by definition, no farther than a 10-km radius) may be primarily along the repository level flowtop, or may transect multiple-repeating basalt flows and interbed strata. Thus, quantified descriptions of radionuclide behavior in the presence of basalt primary minerals, secondary minerals, and interbed materials, in conjunction with representative groundwaters under expected repository physicochemical parameters, are needed to support radionuclide release calculations for each of the pathway steps. This represents a relatively complex geologic and geochemical system. The BWIP radionuclide sorption information has been sorted in the following sections and summarized for each of these discrete modeling pathway steps, insofar as was possible.

### 3.2 GEOLOGIC MATERIALS

The following sections discuss information on the basalt primary and secondary phases, interbed materials, and groundwaters.

#### 3.2.1 Basalt Primary Phases

Three pulverized basalt materials have been used in the experimental work to measure radionuclide sorption on relevant basalts. These are Umtanum (the reference repository level), Pomona, and Flow E basalts. A basalt called Sentinal Gap in some earlier reports is probably the same as Flow E. All of these were obtained from rock outcrops or construction tunnels. No sorption work was done with drill core samples. [The characterization of drill core samples has been reported (BENSON and TEAGUE 1979)]. The following reports describe sorption measurements with these basalts:

<u>Umtanum</u>	<u>Pomona</u>	<u>Flow E</u>
Ames and McGarrah 1981a	Ames and McGarrah 1981a	Ames and McGarrah 1981a
Ames and McGarrah 1981b	Ames and McGarrah 1981b	Ames and McGarrah 1981b
Ames 1982	Ames 1982	Ames 1982
Barney 1981b	Salter 1981b	Barney 1981a
SCR 1982		Relyea and Serne 1979
Salter and Jacobs 1981		Salter 1981b
Salter 1981b		

A number of these reports compile information from preceding reports, so some of the information is repeated.

A comparison of the three basalts is given in Salter et al. (1981b). The mineralogy reported is:

	<u>Umtanum</u>	<u>Pomona</u>	<u>Flow E</u>
Plagioclase	26%	34%	46%
Pyroxene	21%	31%	32%
Secondary minerals	8%	6%	5%
Metallic oxides	7%	6%	3%
Groundmass (glass)	38%	23%	14%

The bulk chemical composition for the three basalts, as well as physical properties, is very similar; the greatest difference seems to be in the degree of crystallization (groundmass fraction) and the crystalline phases formed.

An extensive description of the characterization of two Umtanum basalt samples is given in the Appendix of Ames and McGarrah 1981a. These were outcrop materials from Priest Rapids and Sentinel Gap. The differences observed between the two were reported to be relatively minor.

### 3.2.2 Basalt Secondary Phases

Some radionuclide sorption work has been carried out at BWIP with secondary minerals recovered from isolated vugs. The key reference (SALTER 1981a) describes the recovery of 10 kg of secondary minerals from the Pomona basalt. The material was characterized as primarily (98%) smectite clays. The same secondary mineral material was used for sorption data reported in Salter et al. (1981a), Ames and co-workers (1982), and Barney (1981a). Some radionuclide sorption data for "secondary minerals" were also reported by Ames and McGarrah (1981a), but the source of the minerals was not identified. An extensive description of secondary mineral characteristics is given in Benson and Teague (1979); that material was from drill core samples and was not used in the sorption tests.

Benson and Teague (1979) indicated that secondary minerals contain approximately equal amounts of smectites and clinoptilolite, and lesser amounts of silica. The sorption work (SALTER 1981a) reports data only for a sample containing smectites.

The Site Characterization Report (SCR 1982) reports radionuclide sorption data (Table 6-20) for secondary minerals, but the source of the minerals was not identified. Earlier sections of the Site Characterization Report (1982) give a summary of the site primary and secondary mineralization.

### 3.2.3 Interbed Materials

Only limited work has been done at BWIP to measure radionuclide sorption on interbed materials. The primary reference is Barney (1982). Two materials, sandstone and tuff, located in the Rattlesnake Ridge Interbed, were used. These were mineralogically characterized as follows:

Sandstone

Quartz  
 Plagioclase  
 Orthoclase  
 Hornblende  
 Muscovite  
 Biotite  
 Clinopyroxene

Tuff

Smectite Clay  
 Glass

Sorption data for interbed materials from an undefined source are given in the Site Characterization Report (1982). Data for Mabton interbed materials are shown in Salter and Jacobs (1981). The Mabton interbed materials were not further described or characterized.

Extensive information on radionuclide migration in Hanford Reservation surface soils is reported in Routson et al. (1981a, 1981b). This information may be relevant to interbed migration because of the similar geologic development of the materials.

3.2.4 Groundwaters

Almost all of the sorption work has been carried out with the following two synthetic groundwaters that are reported to be characteristic of the major chemical compositions of in situ groundwater: (1) GR-1, representative of Saddle Mountain and the upper basalts; and (2) GR-2, which simulates groundwater in the Grande Ronde basalts. Their compositions are:

<u>Species</u>	<u>GR-1</u> <u>(mg/L)</u>	<u>GR-2</u> <u>(mg/L)</u>
Na <sup>+</sup>	30.7	225
K <sup>+</sup>	9.0	2.5
Ca <sup>2+</sup>	6.5	1.06
Mg <sup>2+</sup>	1.0	0.07
Cl <sup>-</sup>	14.4	131
CO <sub>3</sub> <sup>2-</sup>	0	59
HCO <sub>3</sub> <sup>-</sup>	81.5	75
F <sup>-</sup>	0	29
SO <sub>4</sub> <sup>2-</sup>	11.1	72
SiO <sub>2</sub>	25	108
pH	8.0	10.0

In some sorption experiments, 0.05 or 0.1 M hydrazine was added to the groundwater to attempt to simulate reducing repository conditions expected by BWIP (BARNEY 1982; SALTER 1981b; and SCR 1982). No sorption work was reported using actual site groundwater samples, nor was there discussion concerning the limitations of using exogenous materials, such as hydrazine, to simulate repository redox conditions.



No reports describing radionuclide sorption measurements with groundwaters altered by thermal and/or radiolytic reactions expected in the repository near field were identified. Possible alteration of the groundwater composition during the high-temperature/high-pressure tests was not discussed (AMES and MCGARRAH 1981b). No groundwaters representative of interbed aquifers were described.

### 3.3 EXPERIMENTAL METHODS AND PARAMETERS

The following sections detail the results of low-temperature and high-temperature/high-pressure batch radionuclide sorption tests.

#### 3.3.1 Low-Temperature Tests

Most of the radionuclide sorption data for the BWIP have been obtained by batch contact techniques. The experimental methods and parameters are summarized in the three key documents: Salter et al. (1981b) for basalt, Salter et al. (1981a) for secondary minerals, and Barney (1982) for interbed materials. The batch contact parameters used were:

	<u>Salter et al. (1981b)</u>	<u>Salter et al. (1981a)</u>	<u>Barney (1982)</u>
Equipment	50-mL polycarbonate tube	Same	Same
Solids	3 g	3 g	1 and 3 g
Solution	30 mL	30 mL	30 mL
Agitation	60 epm <sup>a</sup>	60 epm	60 epm
Temperature	23 ± 2°C	23 ± 2°C	23°C
	60 ± 0.5°C	60 ± 0.5°C	60°C and 80°C
Time	60 d	60 d	14 d
Separation	Amicon filter	Amicon filter	Amicon filter
Oxic	Yes	Yes	Yes
Anoxic	Yes	No	Yes

<sup>a</sup>epm = excursions per minute.

A discussion of the possible effects of the test parameters on the radionuclide sorption values measured is given in Barney (1981a) and Serne and Relyea (1982). The application of column chromatographic methods to confirm batch test distribution coefficients is discussed by Serne and Relyea (1982). No BWIP column test results were identified in the reports reviewed.

### 3.3.2 High-Temperature/High-Pressure Tests

A series of tests to explore the effect of high temperatures/high pressures on the measured radionuclide sorption behavior on basalt was carried out (AMES and MCGARRAH, 1981a, 1981b and SALTER 1981b). The same experimental apparatus was used in each case. A 300-mL Inconel pressure vessel was used for tests at 150°C and 300°C. A Teflon liner was used at the lower temperature to limit radionuclide sorption/reaction with the Inconel metal. The 25 g of basalt and 250 mL of synthetic groundwater containing the radionuclide were placed in the vessel. The vessel was sealed and purged with argon, and then held at the desired temperature for 4 to 8 weeks without agitation. Liquid samples for analysis were withdrawn at various times through a cooled sample line.

### 3.4 SORPTION DATA TREATMENT

The following two sections discuss the distribution coefficient data and the sorption isotherms that describe radionuclide sorption.

#### 3.4.1 Distribution Coefficient Data

A review of the status of radionuclide sorption measurement technology is given in Barney (1981b) and Serne and Relyea (1982). Both batch contact tests and column chromatographic methods can be utilized to measure radionuclide sorption values. The reports reviewed show that the BWIP program has utilized only batch methods. The measured ratio of adsorbed radionuclide concentration divided by radionuclide concentration in solution should be called a "sorption ratio," unless it has been established that sorption-desorption equilibrium has been attained in the test, in which case, the measured value is the "distribution coefficient,"  $K_d$  (see Sect. 4.1). No BWIP reports describing desorption tests were identified, thus all the BWIP data reported as distribution coefficients are actually sorption ratios. Multiple speciation effects, which could have a major impact on the measured radionuclide distribution coefficient(s), can be detected only by column chromatographic methods, and such tests were not identified in the BWIP reports covered in this review.

#### 3.4.2 Sorption Isotherms

Tabulation and utilization of single radionuclide distribution coefficient values does not reveal the effect of radionuclide concentration on the sorption behavior (SERNE and RELYEA 1982). Sorption isotherm plots and mathematical representations are used to express the radionuclide concentration effect on sorption behavior. Linearized isotherms are desired for inclusion in migration analysis computer codes. A number of the BWIP documents reviewed report both Freundlich isotherm data and Dubinin-Radushkevich isotherm parameters for some radionuclides (AMES and MCGARRAH 1981a; AMES 1982; BARNEY 1982; SCR 1982; SALTER 1981b).

### 3.5 SUMMARY OF RADIONUCLIDE SORPTION INFORMATION

A brief summary of the information reported by BWIP for the key radionuclides of interest or concern for a high-level waste repository in basalt is given in this section. The key radionuclides are listed in sequence of decreasing hazard as identified by Barney and Wood (1980). The ranking was based on quantity of radionuclides in the stored waste, biological toxicity, leach rate of the wastes into groundwater, and transport via groundwater. The radionuclide sorption data for the key radionuclides were taken primarily from the three key reports: Salter et al. (1981b) for basalt, Salter et al. (1981a) for secondary minerals, and Barney (1982) for interbed materials. Information from the Site Characterization Report (SCR 1982) was also included because that report represents the most recent evaluated compilation of data prepared by the BWIP.

#### 3.5.1 Technetium

Technetium is considered to be the most hazardous radionuclide in high-level waste.

##### Basalt:

Under oxic conditions, the technetium distribution coefficients,  $K_d$ , of  $26.8 \pm 21.9$ , 0, and 0 mL/g were reported for Umtanum, Flow E, and Pomona basalts, respectively at 25°C, and similar values were recorded for 60°C. No high-temperature/high-pressure data for technetium were reported. Groundwater composition under oxic conditions had only a minor effect on  $K_d$  values; Umtanum basalt always gave moderate distribution coefficients while Pomona or Flow E basalts gave  $K_d$  values of 0. Under reducing conditions (i.e., hydrazine added) higher technetium  $K_d$  values were obtained, but it was suggested that this may be due to insolubilization of technetium as a  $TcO_2$  precipitate. Conservative best-estimate  $K_d$  values for  $^{99}Tc$  of 0 mL/g under oxidizing conditions and 29 mL/g under reducing conditions were given in Salter and co-workers (1981b), and these values were repeated in the Site Characterization Report (1982). No technetium sorption isotherms were identified.

##### Secondary minerals:

Technetium  $K_d$  values of 0 mL/g were obtained with secondary minerals under oxic conditions at 23°C and 60°C with either groundwater (SALTER 1981a). In the Site Characterization Report (1982),  $^{99}Tc$   $K_d$  values of 0 mL/g under oxidizing conditions and 50 mL/g under reducing conditions were reported. The source of the reducing condition value was not identified. No sorption isotherms were identified.

Interbed materials:

Freundlich isotherm plots for technetium sorption on sandstone were reported for 23°C and 60°C under oxidizing and reducing conditions; distribution coefficient data for tuff were also given (BARNEY 1982). Average Kd values of  $104 \pm 66$  and  $46 \pm 7$  mL/g for sandstone and tuff, respectively, under reducing conditions (i.e., hydrazine added), and  $1.8 \pm 2.4$  and  $2.8 \pm 2.2$  mL/g under oxidizing conditions were reported. The Site Characterization Report (1982) gave conservative best estimates for technetium sorption on interbed materials of 0 mL/g under oxidizing conditions and 70 mL/g under reducing conditions.

3.5.2 Iodine

Iodine is considered the second most hazardous radionuclide.

Basalt:

Under oxidizing conditions, Umtanum, Flow E and Pomona basalts gave, respectively,  $^{125}\text{I}$  Kd values of  $6.8 \pm 1.3$ ,  $1.0 \pm 0.4$ , and 2.0 at 23°C. At 60°C and 125°C, Kd values of 0 mL/g were obtained, except for Flow E which gave  $3.4 \pm 4.7$  mL/g. The effect of groundwater composition or reducing conditions was not tested. No sorption isotherms were identified. A current best estimate of  $^{125}\text{I}$  Kd of 0 mL/g for oxidizing conditions was given in Salter (1981b) and repeated in the Site Characterization Report (1982). No value was given for reducing conditions.

Secondary minerals:

Kd values of  $14.0 \pm 1.8$  and 0 mL/g at 23°C and 60°C, respectively, for secondary minerals were reported (SALTER 1981b). The effect of groundwater composition or reducing conditions was not investigated. No sorption isotherms were given. The Site Characterization Report (1982) gave conservative best estimates of  $^{125}\text{I}$  Kd of 0 mL/g for oxidizing conditions and no value for reducing conditions.

Interbed materials:

No data for iodine were reported (BARNEY 1982).

3.5.3 NeptuniumBasalt:

Distribution coefficients for  $^{237}\text{Np}$  of  $30 \pm 13$ ,  $4.1 \pm 0.9$ , and  $9.8 \pm 0.5$  mL/g were reported for Umtanum, Flow E, and Pomona basalts, respectively, under oxidizing conditions (SALTER 1981b). Similar values were obtained at 60°C; no data were reported for 150°C. The groundwater composition had a significant effect on the measured Kd values. Under reducing conditions,

dramatically higher Kd values were obtained, reportedly due to reduction of Np(V) to Np(IV). Current best estimates for  $^{237}\text{Np}$  of 15 mL/g under oxidizing conditions and 200 mL/g under reducing conditions were given; the respective values used in the Site Characterization Report (1982) were 10 and 200 mL/g. No sorption isotherms were reported.

#### Secondary minerals:

Distribution coefficients of  $36.9 \pm 7.5$  and  $53.5 \pm 18.8$  mL/g for  $^{237}\text{Np}$  and secondary minerals at 23°C and 60°C, respectively, were reported (SALTER 1981a). As for basalt, the groundwater composition had a significant effect. Conservative best estimates of 50 and 200 mL/g for  $^{237}\text{Np}$  under oxidizing and reducing conditions, respectively, were given in the Site Characterization Report (1982). The source of the reducing condition value was not identified.

#### Interbed materials:

Distribution coefficients for  $^{237}\text{Np}$  onto sandstone and tuff varied considerably (low of  $13 \pm 3$  to high of  $600 \pm 70$  mL/g), depending on the groundwater composition and presence or absence of hydrazine (BARNEY 1982). The Site Characterization Report (1982) conservative best estimates were Kd values of 20 and 50 mL/g, respectively, for oxidizing and reducing conditions.

### 3.5.4 Radium

#### Basalt:

The sorption of radium was similar for all basalts, and gave Kd values of 127 to 187 mL/g at 23°C and 313 to 399 mL/g at 60°C. No data were reported at 150°C. Neither groundwater composition nor reducing conditions had a significant effect on the Kd values. Radium sorption fit a Freundlich isotherm format. A conservative best estimate of a  $^{226}\text{Ra}$  Kd of 200 mL/g under oxidizing conditions was given (SALTER 1981b) and repeated in the Site Characterization Report (1982). No value was given for reducing conditions.

#### Secondary minerals:

Radium Kd values of  $102 \pm 2$  and  $146 \pm 39$  mL/g at 23°C and 60°C, respectively, were given in Salter (1981a). A current conservative best estimate of 100 mL/g under oxidizing conditions was given in the Site Characterization Report (1982). No data under reducing conditions or sorption isotherms were identified.

#### Interbed materials:

High radium distribution coefficients were obtained for either sandstone

or tuff under all groundwater compositions tests and under both oxidizing and reducing conditions (BARNEY 1982).  $K_d$  values ranged for a low of  $1400 \pm 300$  to a high of  $7200 \pm 2800$  mL/g. Radium sorption data for sandstone fit a Freundlich isotherm format. Conservative best estimates for  $^{226}\text{Ra}$  distribution coefficients in the Site Characterization Report (1982) were 4000 mL/g under oxidizing conditions; no estimate for reducing conditions was reported.

#### 3.5.5 Palladium

Palladium was considered to be the fifth most hazardous radionuclide in high-level waste (BARNEY and WOOD 1980). No palladium sorption data were identified.

#### 3.5.6 Thorium

Thorium was considered to be the sixth most hazardous radionuclide (BARNEY and WOOD 1980). No thorium sorption data were identified.

#### 3.5.7 Lead

Lead was the seventh most hazardous (BARNEY and WOOD 1980). No lead sorption data were identified.

#### 3.5.8 Tin

Tin was the eighth most hazardous (BARNEY and WOOD 1980). No tin sorption data were identified.

#### 3.5.9 Selenium

##### Basalt:

Selenium gave low distribution coefficients of  $5.4 \pm 1.3$ ,  $1.2 \pm 0.3$ , and  $2.4 \pm 0.7$  mL/g, respectively, for Umtanum, Flow E, and Pomona basalts at 23°C under oxic conditions (SALTER 1981b). At 60°C the  $K_d$  values decreased to 0 to 1 mL/g, while at 150°C much higher values of 91 to 118 mL/g were obtained for Umtanum and Flow E basalts. Groundwater composition or reducing conditions had only a minor effect on  $K_d$  values. Selenium sorption data fit a Freundlich isotherm format. Best-estimate  $K_d$  values of 4 mL/g under oxidizing conditions and 8 mL/g under reducing conditions were given (SALTER 1981b) and repeated in the Site Characterization Report (1982).

##### Secondary minerals:

$K_d$  values of  $7.6 \pm 0.3$  and 0 mL/g, respectively, were reported for 23°C and 60°C (SALTER 1981a) under oxic conditions. The Site Characterization Report (1982) gives  $K_d$  values of 5 mL/g for oxic conditions and 8 mL/g

for reducing conditions. The source of the reducing condition value was not identified. No sorption isotherms were reported.

#### Interbed materials:

Distribution coefficient values for  $^{75}\text{Se}$  with sandstone or tuff were all between 1.7 and 5.9 mL/g for all groundwater compositions tested, or under oxidizing or reducing conditions (BARNEY 1982). The conservative best estimates in the Site Characterization Report (1982) were given as 0 and 2 mL/g under oxidizing and reducing conditions, respectively.

#### 3.5.10 Plutonium

Plutonium was the tenth most hazardous radionuclide on the list developed by Barney and Wood (1980).

#### Basalt:

All three basalts tested, Umtanum, Flow E, and Pomona gave  $^{241}\text{Pu}$  Kd values between  $102 \pm 97$  and  $267 \pm 18$  mL/g under oxidizing conditions at  $23^\circ\text{C}$  (SALTER 1981b). The Kd values increased at  $60^\circ\text{C}$  ( $300 \pm 26$  to  $700 \pm 108$  mL/g). Groundwater composition had a significant effect on plutonium Kd values; GR-2 which contained added fluoride gave much lower distribution coefficient values. Plutonium sorption data fit a Freundlich isotherm format. Current best-estimate Kd values (SALTER 1981b) for Pu were 22 mL/g under oxidizing conditions and 42 mL/g under reducing conditions and were repeated in the Site Characterization Report (1982).

#### Secondary minerals:

High plutonium distribution coefficients for  $^{241}\text{Pu}$  of  $2572 \pm 341$  and  $3328 \pm 609$  mL/g were reported for  $23^\circ\text{C}$  and  $60^\circ\text{C}$  (SALTER 1981a). The effect of groundwater composition was not tested, and sorption isotherms were not reported. The Site Characterization Report (1982) gives conservative best-estimate Kd values for plutonium of 2000 and 4000 mL/g for oxidizing and reducing conditions, respectively.

#### Interbed materials:

Data for plutonium sorption on sandstone or tuff gave widely ranging Kd values depending on the groundwater composition and redox condition. Values from  $270 \pm 130$  to  $2570 \pm 1470$  mL/g were reported (BARNEY 1982). No sorption isotherm data were reported. The Site Characterization Report (1982) gave conservative best estimates of 300 mL/g under oxidizing conditions and 470 mL/g under reducing conditions.

### 3.5.11 Uranium

Uranium isotopes were ranked eighteenth ( $^{238}\text{U}$ ), fifteenth ( $^{233}\text{U}$ ), and eleventh ( $^{234}\text{U}$ ) in the hazards list (BARNEY and WOOD 1980). Considerable sorption information has been developed for uranium by the BWIP.

#### Basalt:

Uranium distribution coefficient values of  $56 \pm 11$ ,  $13 \pm 1$ , and  $16 \pm 2$  mL/g for Umtanum, Flow E, and Pomona basalts were reported under oxidizing conditions at 23°C (SALTER 1981b). The Kd values increased dramatically with temperature until values of  $>10,000$  and  $>21,500$  mL/g were obtained at 300°C under oxidizing conditions. It was suggested that this increase might be due to (1) the adsorption of U(VI) on newly formed secondary phases or (2) the precipitation of reduced U(IV) because of a chemical reaction with the basalt. Groundwater composition had a significant effect, and lower Kd values were obtained in the presence of the fluoride ion. Reducing conditions (i.e., added hydrazine) gave higher distribution coefficients. Uranium sorption data were fit to both Freundlich and Dubinin-Radushkevich isotherm formats. Current best estimates of uranium Kd values of 6 mL/g under oxidizing conditions and 40 mL/g under reducing conditions were given (SALTER 1981b) and repeated in the Site Characterization Report (1982).

#### Secondary minerals:

Uranium sorption values were sensitive to both temperature and groundwater composition under oxic conditions (SALTER 1981a). The Kd values for  $^{233}\text{U}$  ranged from  $76 \pm 31$  to  $1450 \pm 297$  mL/g. The uranium sorption data at both 23°C and 60°C for both groundwaters were fit to Dubinin-Radushkevich isotherm plots. Tests under reducing conditions were not reported. The Site Characterization Report (1982) gives a conservative best estimate for  $^{233}\text{U}$  Kd of 70 mL/g under oxidizing conditions.

#### Interbed materials:

Uranium sorption data were plotted as Freundlich isotherms for sandstone at 23°C, 60°C, and 85°C (BARNEY 1982). The Kd ranges were 30 to 40 mL/g at 23°C, 100 to 300 mL/g at 60°C, and 60 to 300 mL/g at 85°C. Uranium sorption was not reported for tuff and was not tested under reducing conditions. The Site Characterization Report (1982) shows "no data available" for uranium.

### 3.5.12 Cesium

Cesium-135 was ranked fifteenth in the hazards ranking (BARNEY and WOOD 1980).



Basalt:

High distribution coefficients were reported (SALTER 1981b) for Umtanum, Flow E, and Pomona basalts; Kd values ranged from  $578 \pm 6$  to  $1685 \pm 245$  mL/g under oxidizing conditions at 23°C. Similar values were measured at 60°C while lower values were obtained at 150°C. Groundwater composition had little effect on cesium sorption. The cesium sorption data at both 23°C and 60°C were fit to Dubinin-Radushkevich isotherm plots. A current best estimate value for a  $^{137}\text{Cs}$  Kd of 500 mL/g was reported (SALTER 1981b) under oxidizing conditions and no value was reported for reducing conditions. The Site Characterization Report (1982) repeated this value.

Secondary minerals:

Kd values for  $^{137}\text{Cs}$  of  $>10,000$  and  $1432 \pm 695$  mL/g were reported for 23°C and 60°C, respectively, under oxidizing conditions (SALTER 1981a). Groundwater composition did not have a major effect on cesium sorption. The Site Characterization Report (1982) gives a conservative best-estimate Kd value for  $^{137}\text{Cs}$  of 5000 mL/g under oxidizing conditions, and no value for reducing conditions.

Interbed materials:

Cesium isotherms for sorption on sandstone under oxic conditions fit a Freundlich isotherm plot (BARNEY 1982). Kd values for  $^{137}\text{Cs}$  sorption on sandstone or tuff as a function of groundwater composition and oxidizing or reducing conditions ranged from  $1000 \pm 100$  to  $7000 \pm 3000$  mL/g. The Site Characterization Report (1982) gave a conservative best estimate for  $^{137}\text{Cs}$  Kd of 2200 mL/g under oxidizing conditions and no value under reducing conditions.

3.5.13 Americium

Americium-241 was listed eighteenth (tied with  $^{238}\text{U}$ ) on the hazards ranking (BARNEY and WOOD 1980).

Basalt:

Distribution coefficient values of  $277 \pm 103$ ,  $622 \pm 180$ , and  $696 \pm 93$  mL/g were reported, respectively, for Umtanum, Flow E, and Pomona basalts at 23°C under oxic conditions (SALTER 1981b). Similar values were recorded at 60°C. The effects of groundwater composition or reducing conditions were not tested. Sorption isotherms were not reported. A current best estimate for the  $^{241}\text{Am}$  Kd of 340 mL/g was given (SALTER 1981b) and repeated in the Site Characterization Report (1982).

Secondary minerals:

High americium sorption values of  $1355 \pm 152$  and  $1489 \pm 350$  mL/g were reported (SALTER 1981a) at 23°C and 60°C, respectively. The effect of groundwater composition was not reported, nor were sorption isotherms. The Site Characterization Report (1982) gives a conservative best estimate for the  $^{241}\text{Am}$  Kd of 1000 mL/g under oxidizing conditions, and no value under reducing conditions.

Interbed materials:

The limited americium data reported were plotted in a Freundlich isotherm format. Distribution coefficient values for  $^{241}\text{Am}$  sorption on sandstone under oxidizing conditions were 400 to 700 mL/g at 23°C, 1,000 to 3,000 mL/g at 60°C and 4,000 to 10,000 mL/g at 85°C. Sorption on tuff or under reducing conditions was not reported. The Site Characterization Report (1982) gives conservative best estimates for  $^{241}\text{Am}$  Kd values of  $>10,000$  mL/g for both oxidizing and reducing conditions. The source of the reducing condition data was not identified.

3.5.14 Strontium

Strontium-90 was ranked last (twenty-third) in the hazards ranking (BARNEY and WOOD 1980).

Basalt:

Distribution coefficients for  $^{85}\text{Sr}$  of  $91 \pm 5$  to  $121 \pm 9$  mL/g were reported for sorption on Umtanum, Flow E, or Pomona basalts under oxic conditions at 23°C (SALTER 1981b). These values did not change appreciably at 60°C or 150°C. Groundwater composition did not have a major effect; the effect of reducing conditions was not reported. A current best estimate for  $^{85}\text{Sr}$  Kd of 170 mL/g under oxidizing conditions was given (SALTER 1981b) and repeated in the Site Characterization Report (1982).

Secondary minerals:

Strontium Kd values ranged from  $249 \pm 49$  to  $451 \pm 103$  mL/g at 23°C or 60°C and for either groundwater (SALTER 1981a). The sorption data fit a Freundlich isotherm format. The Site Characterization Report (1982) gives a conservative best-estimate  $^{85}\text{Sr}$  Kd value of 200 mL/g under oxidizing conditions and no value for reducing conditions.

Interbed materials:

Strontium sorption on sandstone under oxic conditions at 23°C, 60°C, and 80°C fit a single line on a Freundlich isotherm plot (BARNEY 1982). The  $^{85}\text{Sr}$  Kd values for sandstone or tuff under various groundwater compositions and in the presence or absence of added hydrazine ranged from

400 to 7000  $\pm$  2200 mL/g. The Site Characterization Report (1982) gives a conservative best estimate for the  $^{85}\text{Sr}$  Kd under oxidizing conditions of 340 mL/g, and no value for reducing conditions.

#### 3.5.15 Others

Other key radionuclides identified in Barney and Wood (1980) which have not been studied by BWIP for sorption behavior include  $^{93}\text{Zr}$ ,  $^{245}\text{Cm}$ ,  $^{87}\text{Rb}$ , and  $^{166}\text{mHo}$ .

#### 4. INFORMATION ASSESSMENT

The following sections present an assessment of sorption information relevant to the Umtanum basalt, upper basalt layers, and interbed regions of the BWIP site which was available as of May 1983. Included is an assessment of the adequacy and accuracy of the sorption information, the radionuclides studied, and their relevance to the BWIP sorption issue.

##### 4.1 BWIP SORPTION INFORMATION ADEQUACY AND ACCURACY/PRECISION

In order to adequately assess radionuclide sorption behavior on geologic materials and to obtain distribution coefficient or sorption isotherm data which are conservative and defensible for radionuclide release modeling calculations, it is desirable that the data be obtained under steady-state conditions, and that possible radionuclide multiple speciation effects be either eliminated or quantified and treated in the calculations. The laboratory experimental approach to develop data that satisfy these requirements involves three levels of sorption experiments. If the data are not collected under steady-state conditions, it still may be useful for the evaluation of limiting values and bounding conditions.

First, batch tests are run to measure sorption ratios ( $R_s$ ) at various radionuclide concentrations, and the sorption ratio data are fitted to appropriate linearized sorption isotherm formats. Then, second, batch sorption-desorption tests are carried out to test for sorption-desorption disequilibrium. If the desorption ratios measured ( $R_d$ ) are equivalent to the sorption ratios, then the system is at, or near, steady state and the sorption ratios are equivalent to distribution coefficients ( $K_d$ ). (i.e.,  $R_s = R_d = K_d$ ). However, for some radionuclides, chemisorption or surface adsorption reactions may lead to large disequilibrium conditions, and desorption ratios may be much larger than sorption ratios. When this occurs, since radionuclide migration in geologic media is essentially a multistage chromatographic process, the desorption ratios will dominate the retardation calculations and should be used to model expected behavior.

Third, many radionuclides can exist as multiple-solution species under geologic conditions (e.g., as several complexes or in more than one oxidation state, due to geologic media-radionuclide reaction stoichiometry and/or kinetic considerations. Each radionuclide species will have a characteristic distribution coefficient and sorption isotherm. If multiple species exist, the radionuclide retardation calculations must model each species separately. Batch tests cannot reveal these multiple-speciation effects, and column chromatographic methods must be utilized to test for the possible existence of multiple species. Column chromatographic tests also are used to confirm radionuclide retardation factors calculated from batch test distribution coefficients.

The BWIP sorption information consists of data acquired only by batch sorption tests. No measurements of desorption ratios were reported. Thus, rigorously, none of the data reported should be called distribution coefficients, and the values should be considered as sorption ratios. In general, sorption-desorption disequilibrium leads to increased radionuclide retardation factors, so lack of knowledge of desorption ratios could be considered as potentially conservative for modeling purposes. However, for some radionuclides this could be unrealistically conservative, and could indicate the existence of marginal or unsatisfactory repository retardation factors for some radionuclides, when, in fact, very favorable retardation behavior would be experienced due to the high desorption ratios.

No column chromatographic experiments to test for and quantify multiple-speciation effects were reported by the BWIP. Most actinide elements and some fission products can form a number of possible complexes with typical groundwater constituents, such as carbonate or fluoride, and in some cases could exist in more than one valence (e.g., plutonium or neptunium). The batch tests reported by BWIP yield only average distribution coefficients, and this would obscure multiple-speciation situations where, for instance, one species is poorly adsorbed, and thus migrates rapidly, while the other species are strongly adsorbed and are practically immobilized. Thus, the BWIP data obtained may be highly unconservative for radionuclide release modeling purposes in some cases.

A discussion of the precision and accuracy of the experimentally measured radionuclide distribution coefficients was not included in the BWIP key sorption data references or in the Site Characterization Report (1982). Much of the data were presented as values plus/minus a standard deviation. Some values had small standard deviations while others had very large deviations (as large as the value itself). It is very difficult to assess this information and develop even a qualitative measure of the data precision and accuracy. Barney (1981b) or Serne and Relyea (1982) do not specifically discuss assessment of precision and/or accuracy. In a controlled sample study (RELYEA and SERNE 1979), many radionuclide distribution coefficient values varied by three orders-of-magnitude when measurements were made at different laboratories; it was concluded that some experimental parameters were uncontrolled. It seems possible that similar experimental parametric considerations could apply to the BWIP sorption data. For the calculation of conservative radionuclide release calculations, it might be necessary to consider sensitivity analyses, and to reduce the distribution coefficient values below those reported by BWIP for the radionuclides whose release calculations may appear most sensitive to uncertainties in the data. Defensible release calculation may require a better understanding of sorption data accuracy and precision.

#### 4.2 NEAR-FIELD CONDITIONS

The repository near-field will consist of a waste form (glass or spent fuel elements) in a metal canister (possibly steel) which is surrounded by packing material (possibly bentonite or bentonite plus crushed basalt) in a mined cavity that will be backfilled with crushed basalt at some time (repository closure). The temperature in the near field (due to the radioactive decay heat) may be from about 200°C to 300°C during the thermal peak, and the pressure may range from ambient to equivalent to the hydrostatic or lithostatic head. The redox conditions will be initially oxidizing due to the air introduced during repository mining and operations, but may slowly return to ambient anoxic conditions some time after repository closure. In a groundwater intrusion event after waste emplacement, the initial groundwater composition will be altered because of chemical reactions with the near-field constituents and/or radiolysis reactions. None of the above conditions and parameters have been finalized for the BWIP site.

The BWIP sorption experimental effort has directed only minimal attention to near-field conditions. The high-temperature/high-pressure work (AMES and McGARRAH 1981b) is closest to the possible near-field parameters. This work did not evaluate radiolysis reactions, possible interaction of radiolysis products with radionuclides, or possible reactions of radionuclides or groundwater with bentonite or canister metal. Thus, the distribution coefficients obtained may be limited to applications under oxidizing conditions with crushed basalt backfill (i.e., before closure). The discussion and data treatment in the Site Characterization Report (1982), Chapt. 6, "Geochemistry," do not address near-field conditions or predict radionuclide sorption behavior in the near-field.

It is concluded that the BWIP work reported is not suitable for modeling radionuclide sorption behavior in the near-field. This limitation introduces complications for the far-field analysis, since the radionuclides must first migrate through the near field, and the groundwater composition and radionuclide species and concentrations entering the far field (sometimes called the source term) will be determined by near-field geochemical behavior. The BWIP near-field environment analysis is greatly hampered by the lack of decision or definition of all the near-field components and parameters. Until much of this is resolved, it will remain difficult to design the needed radionuclide sorption experiments and to develop the necessary data for radionuclide release modeling calculations.

#### 4.3 FAR-FIELD CONDITIONS

The BWIP repository far field encompasses a large volume and wide variety of geologic constituents. The far field begins at the end of the near field, or disturbed zone, some tens to hundreds of meters from the waste canister in the undisturbed repository level geologic member. Depending on the release pathway selected or being modeled, it extends along the repository level basalt flow top and/or through the upper basalt beds, the

interbeds, and finally the surface soils to the accessible environment. (The accessible environment, by definition, is no more than a 10-km distance from the repository.) In order to model radionuclide release rates to the accessible environment, it is necessary to mathematically describe the radionuclide sorption behavior, in addition to other calculational inputs, for each of the possible release pathway units. For the purposes of this sorption information assessment, the release pathway was considered to consist of three distinct geologic components: Umtanum basalt (the reference repository level), upper basalts, and the interbeds. The upper basalts and interbeds are interlayered in a complex sequence.

#### 4.3.1 Umtanum Basalt

The geochemical environment in the Umtanum basalt is summarized in Salter and Jacobs (1981). The report concludes that the geochemical parameters will be:

	<u>Ambient</u>	<u>Expected range</u>
Temperature	59°C	59°C to 300°C
Pressure	114 bars	1 to 114 bars
Groundwater: pH	9.6	6.0 to 9.6
Eh	-0.48 V	+0.5 to -0.61 V
composition	GR-2	

The reported range of expected geochemical parameters in the Umtanum basalt show considerable uncertainty as to the conditions to be encountered. The BWIP radionuclide sorption data are reviewed in the following paragraphs with respect to the data relevance to these expected repository parameters.

#### Temperature:

The bulk of the radionuclide sorption data has been collected at 23°C and thus is not directly relevant to repository modeling needs. Some effort has been made to evaluate the effect of temperature on distribution coefficient values, and this is summarized in the Site Characterization Report (1982). Some radionuclide K<sub>d</sub> values are dramatically affected by temperature changes, while others are less sensitive. Thus, a decision as to whether data collected at 23°C is suitable for modeling purposes at higher temperatures will have to be made on a case-by-case basis. Sufficient BWIP data may be available to permit some calcula-

tions at 60°C. The data for still higher temperatures are extremely limited and there seems to be insufficient information to permit any description of radionuclide sorption behavior at higher temperatures.

#### Pressure:

Only a limited amount of data (AMES and McGARRAH 1981b is the only high-temperature/high-pressure report) are available to support modeling at the 114-bar pressure expected. The effect of pressure is not discussed in the Site Characterization Report (1982). The modeling of radionuclide retardation under realistic repository pressures seems not to be possible from the available data base.

#### Redox conditions:

The redox condition in the far field has been calculated by BWIP to be strongly reducing. This calculation was based on knowledge of the secondary mineral assemblage in basalt, particularly the presence of pyrite. Field measurements of groundwater have never given Eh values as low as those calculated, so the calculated value must be considered unconfirmed. Admittedly, field measurement of Eh is not easy, so failure to obtain measured values which agree with calculated values cannot be taken as precluding the validity of the calculated value. A greater concern with regard to validity or applicability of the calculated Eh value to predict groundwater redox conditions is the fact that pyrite is a minor component of the basalt and chemical communication between the pyrite and the groundwater may be limited. The pyrite may be surrounded by the basalt major minerals, and the basalt fractures and fissures (the groundwater flow path) are lined with secondary minerals which may further isolate the pyrite from the groundwater. At the present time, the use of any particular Eh value to represent far-field redox conditions may be questionable.

BWIP was faced with the problem of reproducing the strongly reducing redox condition which they expect to exist in the repository in their laboratory sorption experiments. They chose to add hydrazine hydrate, a strongly reducing chemical, to the synthetic groundwaters. We have expressed serious concerns relative to the addition of hydrazine hydrate for this purpose (KELMERS 1984). The more important concerns are: (1) the reaction between hydrazine and any reducible radionuclide is undefined, thus the effective redox condition is unknown; (2) hydrazine hydrate dissociation to release hydroxide anions likely dominates the groundwater pH, so the pH no longer is representative of in situ conditions; (3) hydrazine could react with bicarbonate in the groundwater to form the carbamate anion, which may form radionuclide complexes; (4) hydrazine is an aggressive chemical and attacked polycarbonate test tubes as used in the BWIP tests,



causing failure of the tubes or brown-colored degradation products in the groundwater; (5) hydrazine may alter or disaggregate clay mineral structures, and change the secondary minerals in the test; and, (6) considerable uncertainty exists as to the solid phase or solution species formed by the reaction of hydrazine with some radionuclides such as technetium. Thus, we feel it is not possible to assert that use of hydrazine in modeling repository Eh conditions and sorption information collected in the presence of hydrazine may not be considered acceptable for defensible or conservative modeling purposes.

#### Groundwater:

All the sorption tests have been run in the presence of synthetic groundwater GR-2, which is believed to be representative of current Umtanum level groundwater, or synthetic groundwater GR-1, which is representative of upper basalt beds. Since a groundwater-intrusion event scenario has not been selected for modeling purposes, it is not clear that in situ groundwater would be the intruding liquid. Extensive chemical alteration of the intruding groundwater may be expected from thermal reactions with the basalt (especially the chemically reactive groundmass) and radiolysis reactions in the near field. Since migrating radionuclides must start in the near field, it seems possible that the current in situ Umtanum groundwater may not be representative of the migration-event far-field groundwater. No BWIP studies to evaluate the sensitivity of radionuclide distribution coefficients to groundwater composition variations were identified. The limited selection of synthetic groundwaters tested in sorption experiments with Umtanum basalt render the defensibility of the retardation factors to be calculated from this information questionable. No parallel experiments using actual groundwater were reported to confirm the validity of employing synthetic solutions prepared in the laboratory.

#### Mineral selection:

The basalt rocks consist of both primary and secondary minerals and these have been, to a degree, separately evaluated by BWIP. The secondary minerals are concentrated in fissures and vugs, and in the more permeable basalt layer flow tops. Radionuclides in migrating groundwater likely would be exposed to secondary minerals to a greater degree than to the basalt primary minerals since secondary minerals line the probable release pathway. No methods of evaluating or weighting the exposure and accommodation of this phenomenon in radionuclide retardation calculations has been suggested by BWIP. This situation is a major concern, since many radionuclides show quite different, usually higher, distribution coefficients with secondary minerals than with basalt primary minerals. The calculation of defensible radionuclide release rates likely will require resolution of this problem.

#### 4.3.2 Upper Basalt Layers

Much of the BWIP experimental work tests with Flow E and Pomona basalts are in parallel with Umtanum basalt. In general, major differences in radionuclide distribution coefficient values were not observed for many radionuclides, and the Site Characterization Report (1982) discussed all this data as relevant to "Columbia River basalts." While this may be a useful first-level simplification, some radionuclides did show specific differences in sorption behavior with different basalts, perhaps related to the reducing properties of the different basalts. It would seem that caution should be used in generalizing basalt sorption characteristics. It is not obvious that sorption data developed with Grande Ronde basalts can be used to mode migration in upper basalt flows.

All the reservations expressed above (Sect. 4.3.1) for the Umtanum basalt information also apply to data for the upper basalts. In addition, the expected repository geochemical parameters have not been identified for the upper basalt levels, so the data were collected under Umtanum level parameters. Obviously, both the temperature and pressure will decrease at higher levels in the repository.

It seems that insufficient information exists to accurately model radionuclide sorption behavior in the upper basalt layers.

#### 4.3.3 Interbed Regions

The interbed regions in the upper basalt strata of the BWIP site are composed of other rock types (than basalt) and are the locations of major fresh water aquifers. Radionuclides released from emplaced waste that migrates through the Grande Ronde basalt sequence may likely intersect one of the interbed aquifers. The site stratigraphy (SALTER 1981b) shows nine interbed regions. All of these are above the Grande Ronde basalts and are in the Wanapum basalts and Saddle Mountain basalts. From the Grande Ronde - Wanapum interface up, these are identified as the Vantage, Squaw Creek, Quincy, Mabton, Cold Creek, Gable Mountain, Selah, Rattlesnake Ridge, and Levey interbeds. Each of these represents a separate period of inactive magmatic deosition, and weathering. Only generalized compositional information for these interbeds was given in the Site Characterization Report (1982). The composition of the interbed aquifers was not discussed.

Radionuclide sorption data are reported only for two components, sandstone and tuff, from one interbed, Rattlesnake Ridge (BARNEY 1982). The geochemical parameters to be expected in this or any other interbed aquifer were not identified. Some radionuclides gave very high distribution coefficients on the sandstone and tuff and, thus, the interbeds could be important units in radionuclide migration retardation. This factor could be significant, since the interbed minerals may represent the last significant barrier for radionuclides prior to their release to the accessible environment (The assumption is that radionuclides which remain in solution in an interbed aquifer will move with that aquifer to the environment.).

The information available in Barney (1982) and repeated in the Site Characterization Report (1982), however, seems completely insufficient to accurately assess radionuclide sorption behavior in the BWIP site interbeds.

#### 4.4 RADIONUCLIDES STUDIED

A ranking of key radionuclides of concern for a high-level waste repository in basalt was presented in Barney and Wood (1980). The effort to characterize radionuclide sorption behavior presented in the key documents (SALTER 1981b for basalt, SALTER 1981a for secondary minerals, and BARNEY 1982 for interbed materials) and in the Site Characterization Report (1982) does not correlate with that hazards ranking. The largest amount of distribution coefficient data was collected for uranium, cesium and strontium, which are near the bottom of the hazards ranking. The two radionuclides considered most hazardous,  $^{99}\text{Tc}$  and  $^{129}\text{I}$ , received only limited sorption experimental evaluation, while four of the radionuclides in the ten most hazardous category ( $^{197}\text{Pd}$ ,  $^{230}\text{Th}$ ,  $^{210}\text{Pb}$ , and  $^{126}\text{Sn}$ ) were not investigated in any experiment identified.

The lack of consistency between the BWIP-published radionuclide hazards ranking and the experimental development carried out is not explained. It would seem desirable and reasonable for the BWIP sorption information work effort to reflect a relationship with the importance of the radionuclides tested.

#### 4.5 RELEVANCE TO THE BWIP SORPTION BARRIER

The single goal of the entire experimental sorption program at BWIP is to ultimately gather the data needed to decide whether the site meets all legal requirements for a high-level waste repository as a result of the multiple barriers present. An important part of this effort is to show that in a groundwater-intrusion/groundwater-migration event, radionuclides solubilized from the waste form are adequately retarded from reaching the accessible environment. Sorption of dissolved radionuclides on repository host rock phases is expected to be a major release barrier. In order to model this retardation process and to develop defensible calculated retardation factor values, it is necessary to have input data that quantify radionuclide sorption (distribution coefficients and/or sorption isotherms) onto the migration pathway rock phases under the anticipated repository geochemical parameters. Data that accurately model repository sorption behavior can be used for calculations which predict expected radioactivity release rates, or limiting values can be used to estimate bounding values for release rates. The radionuclide sorption data must be experimentally measured in laboratory tests under site-relevant test parameters. Successful achievement of this presupposes that the release pathway being modeled is defined, the geochemical parameters are established, and that samples of all relevant geologic materials are available for the laboratory tests. At the BWIP site, most of these experimental prerequisites have yet to be satisfied, thus the laboratory effort to measure radionuclide sorption values has been handicapped from the start.

The sorption distribution coefficient and isotherm data developed and reported for the BWIP seem deficient for modeling purposes for the following reasons:

1. The BWIP expects the far field to always be under strongly reducing conditions and for the near field to return to such conditions after repository closure. Much of the radionuclide sorption data was collected under oxic (air present) conditions. Such data might be useful for conservative modeling purposes, but BWIP has not taken such a bounding condition approach. The remainder of the sorption data was collected in the presence of added hydrazine. We doubt if such data can be proven valid for modeling purposes. Thus, no sorption information has been collected under redox conditions that are obviously relevant to the repository near field or far field. This lack of information in this area seems to be a major data deficiency.
2. Most of the data have been collected under ambient temperature and pressure conditions, although the near-field and/or far-field environment are expected to be at elevated temperatures and pressures.
3. The accuracy and precision of the distribution coefficient data reported were not discussed.
4. Only limited information,(or no information) has been collected for some of the reportedly hazardous radionuclides.
5. The synthetic groundwater used in the tests may not be representative of the intrusion-event water, nor has it been shown that synthetic solutions yield the same sorption values as actual groundwater.
6. The possible alteration of groundwater due to chemical reactions with the basalt, packing, and canister, and radiolysis reactions in the near field was not evaluated.
7. Potential radionuclide sorption-desorption disequilibrium and/or multiple-speciation effects were not evaluated.
8. The near-field geochemical parameters are too poorly defined to permit determination of the needed experimental test conditions.
9. The far-field geochemical parameters are not adequately defined to allow determination of accurate and defensible experimental test conditions. It may be possible to determine bounding conditions, but this approach was not discussed.
10. The groundwater migration pathway(s) through the complex BWIP site basalt and interbed layers is not defined, thus it cannot be shown that radionuclide sorption data have been collected for all the necessary geologic components. The data for basalts seem less than adequate, and the information for the interbed materials may be wholly inadequate for modeling purposes.

## 5. ADDITIONAL INFORMATION NEEDS

In Sect. 4, "INFORMATION ASSESSMENT," a number of deficiencies of the radionuclide sorption information needed to support radionuclide release calculations for performance modeling of the BWIP candidate high-level waste repository were identified. Additional information needs that may be needed to address these are summarized in the following sections.

### 5.1 REDOX CONDITIONS

Emphasis has been given by BWIP to the strongly reducing environment expected in the the repository near field or far field (SCR 1982, SALTER 1981a). As discussed above, all of the radionuclide sorption experiments have been carried out either in the presence of air or added hydrazine. Neither of these test conditions adequately simulated repository conditions. We are concerned (KELMERS 1984) whether any added chemical can be used to satisfactorily simulate the basalt/groundwater system redox condition. A more direct approach would be to allow the basalt (or interbed) minerals to establish a "natural" redox condition in the tests. This could be accomplished by conducting tests isolated from air in a suitable controlled atmosphere chamber. Such tests might require the preparation of the crushed rock and groundwater as well as conduction of the batch contact tests in the controlled atmosphere chamber in order to achieve the very low oxygen concentrations equivalent to the calculated Eh values. An argon or argon-plus-hydrogen atmosphere might be required in the chamber.

Confirmation of the calculated redox values for the in situ Umtanum groundwater will not be simple, but it seems desirable to attempt to obtain direct Eh measurements. The Umtanum is mineralogically complex and if dominant minerals such as pyrite are not in chemical communication with the groundwater, the calculated Eh value could be seriously misleading. Down-hole redox measurements could be considered, but the values may be complicated by the limited quantity of groundwater in the Umtanum and by possible borehole contamination with drilling muds and detergents. Resolution of this redox condition question may require additional testing after completion of the exploratory shaft to the repository level.

The current uncertainty with respect to near-field and far-field Eh could be, to some extent, circumvented with a sorption test program designed to explore limiting values and bounding conditions. Many radionuclides are not reducible to lower valences and the sorption values measured might be shown to be independent, or only have a low dependence, on the test redox condition. For such radionuclides exact reproduction of the repository Eh might not be important. Even the radionuclides that may be expected to undergo valence changes could be explored under the bounding condition approach. Exploration of the need for accurate sorption data vs limiting values could help simplify the needed information.

## 5.2 ELEVATED TEMPERATURE

Temperatures are expected to be as high as 200°C to 300°C in the near field, while the ambient far-field temperature in the Umtanum is 59°C (SALTER and JACOBS 1981). Thus, all radionuclide sorption reactions in the repository will be at temperatures considerably above laboratory ambient (23°C), where most of the experimental work has been carried out. Some BWIP effort has been directed toward radionuclide sorption measurements at 60°C; however, it may not be possible to generalize the sorption behavior changes to be expected at elevated temperatures, and considerably more high-temperature experimental work may be necessary with the basalts, secondary minerals, and interbed materials. Measurements at elevated temperature under relevant reducing conditions seem especially deficient. Very little work has been reported at temperatures between 200°C and 300°C (i.e., near-field conditions), and this subject was not well-addressed in the Site Characterization Report (1982).

Radionuclide distribution coefficients and sorption isotherms are needed for temperatures up to 300°C. Such tests may require use of an autoclave in a controlled-atmosphere glovebox to achieve both the desired temperature and redox conditions. These experiments may not be simple to conduct, but they seem critical to modeling near-field behavior and to the prediction of both radionuclide concentrations and groundwater compositions that can be expected to migrate from the near field into the far field. Without this information, some far-field test parameters, the sorption information developed, and the performance modeling effort may remain uncertain.

## 5.3. ACCURACY AND PRECISION

No treatment of data accuracy and precision was identified in BWIP reports. It seems essential that such data analysis be conducted for modeling purposes. Accuracy and precision ranges should be utilized in sensitivity analyses of calculated radionuclide release rates to the accessible environment. Some radionuclides may require very accurate and defensible data values, while others could be successfully modeled using limiting values and bounding calculations.

## 5.4 RADIONUCLIDE HAZARDS RANKING

A radionuclide hazards ranking was given in Barney and Wood (1980) for a BWIP repository; however, the BWIP experimental effort did not follow this sequence. It would seem logical to devote the greatest effort to those radionuclides which are ranked potentially most hazardous. The greatest BWIP sorption data development effort was devoted to radionuclides that were low in hazards ranking, and some of the more hazardous radionuclides were never tested. It would seem desirable to reexplore the entire issue of potential radionuclide release hazards and to refocus the experimental program on those of highest ranking.

## 5.5 GROUNDWATER COMPOSITION

Much of the radionuclide sorption measurement work was conducted with one or two synthetic groundwaters. Synthetic groundwaters were used because of the difficulty of obtaining actual well-water samples from the Umtanum. A groundwater-intrusion event scenario has never been defined, however, so it seems uncertain that ambient Umtanum groundwater would necessarily be representative of the intruding water. Intrusion by more plentiful interbed aquifers or other water sources is conceivable. Radionuclide sorption behavior could be quite different in different groundwaters. Also, the potential contamination of the borehole water samples from the Umtanum by drilling muds and detergents has not been conclusively eliminated, and there may be room for concern over possible contamination of the Umtanum groundwater withdrawn from the borehole for analysis.

Limited experimental work to evaluate the sensitivity of radionuclide sorption data to groundwater compositional changes was reported only for interbed materials (BARNEY 1982). It could be desirable to address the question of what chemical composition(s) may be representative of an intruding groundwater, and to design an experimental test matrix that encompasses likely compositions. This may be particularly important for radionuclides that can form stable complexes with trace groundwater constituents such as fluoride, or react with constituents such as ferrous ion.

## 5.6 ALTERED GROUNDWATER

Substantial chemical alteration of the intruding groundwater composition may occur under the near-field thermal and radiolytic conditions, and this altered groundwater, in turn, would migrate to the far field. This has not been well addressed in the BWIP reports identified. Accelerated chemical reactions at higher temperatures involving (1) reactive basalt components such as the groundmass and (2) radiolysis reactions involving groundwater components seem likely and could lead to a substantial alteration of the groundwater chemical composition. This change in composition could have a major effect on the radionuclide chemical speciation and sorption behavior. It would seem that this question should be addressed. As with comments in the preceding sections, it is not completely obvious that the BWIP sorption experimental work has been conducted with the most relevant groundwater(s).

## 5.7 SORPTION-DESORPTION DISEQUILIBRIUM AND MULTIPLE-SPECIATION EFFECTS

Measurement of sorption-desorption disequilibrium or multiple-speciation effects, and thus proof that the reported distribution coefficient values were obtained at a steady-state condition for a single identified radionuclide species (and are, therefore, valid as input data for accurate radionuclide retardation factor calculations), was not

identified in the BWIP reports. This lack of data in this area represents a major source of uncertainty in the sorption values reported. Additional experimental work to address this question may be highly desirable.

#### 5.8 NEAR-FIELD PARAMETERS

All of the near-field geochemical parameters are poorly defined, since the waste form, waste load, container material, buffer material, and backfill material, as well as repository closure time, have not been finalized. This lack of defined geochemical parameters is a major problem in designing relevant experiments and in evaluating the usefulness and validity of the data obtained from experiments. It would seem that a useful approach to such a situation would be to investigate the sensitivity of the data to the potential ranges of parameters that may be relevant or encountered in the repository by running tests under a range of conditions. Such an analysis and evaluation of the near field has not been identified in BWIP reports.

#### 5.9 FAR-FIELD PARAMETERS

The far-field geochemical parameters relevant to a groundwater-intrusion/ groundwater-migration event have not been thoroughly established, including the migration flow path, and this leaves room for concern over the validity of the test parameters selected for the BWIP sorption experimental work and the sorption values obtained. This deficiency stems mainly from lack of consideration of altered groundwater (see Sects. 5.5 and 5.6) and lack of definition of the release pathway to be modeled (see Sect. 5.10).

#### 5.10 RELEASE PATHWAY

The purpose of the experimental sorption program is to gather the data needed to model the radionuclide transport to be expected under various groundwater-intrusion/groundwater-migration event scenarios. To successfully achieve this, defensible, quantified values for many repository aspects are required, including radionuclide retardation factors. Experimental development of the required modeling input values involves laboratory sorption tests with all release pathway geologic components under relevant test parameters. A BWIP defined release pathway(s) has not been identified. Therefore, it can not be asserted that the correct or necessary sorption data have been acquired, or for that matter, that a plan to acquire it can be constructed. It would seem highly desirable to address this concern. Lack of a defined release pathway(s) for modeling purposes may be a major site characterization/assessment uncertainty.



## 6. ACKNOWLEDGEMENTS

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## 7. REFERENCES

The following are the primary references describing radionuclide sorption information for the basalt site issued by the BWIP project, by PNL, or by other DOE laboratories as of May 1983. Papers presented at the National Meeting of the American Chemical Society in Seattle in March 1983 are also included; these papers will likely appear later as RHO-BWI reports. Those references marked with an asterisk (\*) were cited in the BWIP Site Characterization Report.

(\*)AMES 1980. L. L. Ames and J. E. McGarragh, Basalt Radionuclide Distribution Coefficient Determinations: FY 1979 Annual Report, PNL-3146, 1980.

(\*)AMES 1981a. L. L. Ames and J. E. McGarragh, Investigation of Basalt Radionuclide Distribution Coefficients: FY 1980 Annual Report, RHO-BWI-C-108, 1981.

(\*)AMES 1981b. L. L. Ames and J. E. McGarragh, High-Temperature Determination of Radionuclide Distribution Coefficients for Columbia River Basalts, RHO-BWI-C-111, 1981.

AMES 1982. L. L. Ames, J. E. McGarragh, B. A. Walker and P. F. Salter, "Sorption of Uranium and Cesium by Hanford Basalts and Associated Secondary Smectite," Chem. Geol. 35, 205-225 (1982).

AMES 1983. L. L. Ames, P. F. Salter, J. E. McGarragh and B. A. Walker, "Selenium Sorption on a Columbia River Basalt", presented at ACS National Meeting, Seattle, March 1983

(\*)BARNEY 1980. G. S. Barney and B. J. Wood, Identification of Key Radionuclides in a Nuclear Waste Repository in Basalt, RHO-BWI-ST-9, 1980.

(\*)BARNEY 1981a. G. S. Barney, Radionuclide Reactions with Groundwater and Basalts from Columbia River Formations, RHO-SA-217, 1981.

(\*)BARNEY 1981b. G. S. Barney, Evaluation of Methods for Measurement of Radionuclide Distribution in Groundwater/Rock Systems, RHO-BWI-LD-47, 1981.

BARNEY 1982. G. S. Barney, Radionuclide Sorption of Columbia River Basalt Interbed Materials, RHO-BW-SA-198 P, 1982.

BARNEY 1983. G. S. Barney, "Radionuclide Sorption and Desorption Reactions with Interbed Materials from the Columbia River Basalt Formation," presented at ACS National Meeting, Seattle, March 1983.

(\*)BENSON 1979. L. V. Benson and L. S. Teague, A Study of Rock-Water-Nuclear Waste Interactions in the Pasco Basin, Washington, LBL 9677, 1979.

BENSON 1980. L. V. Benson, A Tabulation and Evaluation of Ion Exchange Data on Smectites, Certain Zeolites and Basalt, LBL-10541, 1980.

DELEGARD 1983. C. H. Delegard, G. S. Barney, and S. A. Gallagher, "Effects of Hanford High-Level Waste Components on the Solubility and Sorption of Co, Sr, Np, Pu and Am", presented at ACS National Meeting, Seattle, March 1983.

KELMERS 1984. A. D. Kelmers, J. H. Kessler, W. D. Arnold, R. E. Meyer, N. H. Cutshall, G. K. Jacobs, and S. Y. Lee, Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Volume I, Report for October-December 1983, NUREG/CR-3851, June 1984.

RELYEA 1979. J. F. Relyea and R. J. Serne, Controlled Sample Program Publication Number 2: Interlaboratory Comparison of Batch  $K_d$  Values, PNL-2872, 1979.

ROUTSON 1981a. R. C. Routson, G. S. Barney, R. M. Smith, C. H. Delegard, and L. Jensen, Fission Product Sorption Parameters for Hanford 200 Area Sediment Types, RHO-ST-35, 1981.

ROUTSON 1981b. R. C. Routson, G. S. Barney, and R. M. Smith, "Hanford Site Sorption Studies for the Control of Radioactive Wastes: A Review," Nucl. Tech. 54, 100-106 (1981).

SCR 1982, Site Characterization Report for the Basalt Waste Isolation Project, Chapt. 6. Geochemistry, DOE/RL 62-3, 1982.

SALTER 1981. P. F. Salter and G. K. Jacobs, Evaluation of Radionuclide Transport: Effect of Radionuclide Sorption and Solubility, RHO-BW-SA-192A, 1981.

(\*)SALTER 1981a. P. F. Salter, L. L. Ames, and J. E. McGarragh, Sorption of Selected Radionuclides on Secondary Minerals Associated with the Columbia River Basalts, RHO-BWI-LD-43, 1981.

(\*)SALTER 1981b. P. F. Salter, L. L. Ames, and J. E. McGarragh, The Sorption Behavior of Selected Radionuclides on Columbia River Basalts, RHO-BWI-LD-48, 1981.

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

SHADE 1983. J. W. Shade, L. L. Ames, and J. E. McGarragh, "Actinide and Tc Sorption on Fe-Silicate and Dispersed Clay Colloids," presented at ACS National Meeting, Seattle, March 1983.

VANDEGRIFT 1983. G. F. Vandegrift, D. L. Bowers, T. J. Gerding, S. M. Fried, and M. G. Seitz, "The Interaction of Groundwater and Fresh Basalt Fissure Surfaces and Its Effect on the Migration of Actinides and Fission Products," presented at ACS National Meeting, Seattle, March 1983.

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<b>13. ABSTRACT (200 words or less)</b> <p>This document presents a scientific review and technological assessment of the radionuclide sorption information reported by the Basalt Waste Isolation Project (BWIP) for the candidate high-level waste repository in the Columbia River basalt flows in the Hanford Reservation. Quantified radionuclide sorption data are necessary for repository performance assessment calculations to model expected radioactivity release rates in groundwater intrusion-groundwater-migration scenarios. Three key BWIP reports were identified which contain most of the sorption information for a number of radionuclides with basalt, secondary minerals, or interbed materials. An extended review of these data is presented in this document. The technological assessment identified seven potentially significant deficiencies in the radionuclide sorption information published by BWIP that could lead to questionable or nonconservative radioactivity release calculations. These deficiencies are discussed in the document in detail. Specific additional information needs were also defined and reported.</p>					
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