see folder for Hr.
Edwright & H. OLSON
3-30-84

101.2
(pocket 5)

SD-BWI-TP-022 (WORKSHOP DRAFT) March 5, 1984

Barrier Materials Test Plan

Engineered Barrier Department
Basalt Waste Isolation Project

March 1984

Prepared for the United States
Department of Energy
Under Contract DE-AC06-77RL01030

Rockwell International
Rockwell Hanford Operations
Energy Systems Group
Richland, Washington 99352

8404300195

CONTENTS

APPENDICES:

FIGURES:

TABLES:

1.0 INTRODUCTION

1.1 PROGRAM BACKGROUND

In 1976, the U.S. Energy Research and Development Administration, the predecessor to the U.S. Department of Energy (DOE), established the National Waste Terminal Storage (NWTS) Program. Its mission is to provide multiple repository facilities in various deep geologic formations within the United States for the terminal storage (disposal) of nuclear waste. The Columbia River basalts that underlie the Hanford Site were among those selected for study. Rock types under investigation in addition to basalt are granite, tuff, and bedded and domed salt.

Through the DOE, the NWTS Program is pursuing investigations of several sites where these media exist. Among them are basalt at the Hanford Site and tuff at the Nevada Test Site, both U.S. Government-owned sites. The Hanford Site characterization program is presently the responsibility of the U.S. Department of Energy-Richland Operations Office (DOE-RL). Rockwell Hanford Operations (Rockwell) is the prime contractor responsible for this work. The Basalt Waste Isolation Project (BWIP) within Rockwell has been chartered with the responsibility of conducting the Hanford Site characterization investigations.

Thus, the BWIP mission is to determine if potential geological repository sites exist in basalt under the Hanford Site and to identify and develop the associated facilities and technology (including the design and development of waste packages) required for the permanent isolation of radioactive waste in one of these potential sites. Studies have been conducted to reduce the area being considered for siting of a nuclear waste repository in basalt to a reference repository location in the west-central part of the Hanford Site (Fig. 1-1). Characterization of four candidate basalt flows (the Umtanum, McCoy Canyon, Cohassett, and Rocky Coulee) located beneath the reference repository location is continuing. The Cohassett flow is currently the preferred horizon. Materials screening and testing activities also have been conducted to support the selection of reference materials for development of waste package conceptual designs for disposal in a nuclear waste repository in basalt. Materials testing and analyses needed to support waste package design and performance assessment will continue as described in Section 5.0 of this test plan.

The Design and Development and the Performance Evaluation activities (L24 and L25 of Table 1-1) for waste packages are not included in this draft of the Barriers Materials Test Plan (BMTP). They will be included in the first update of this plan which will be finished by September 30, 1984. The Repository Seal Materials Test Plan now in development also will be updated by September 30, 1984. At that time the two test plans will be combined and become Volume 1, Waste Package and Volume 2, Repository Seals. This test plan will be entitled the Engineered Barriers Test Plan. The other test and

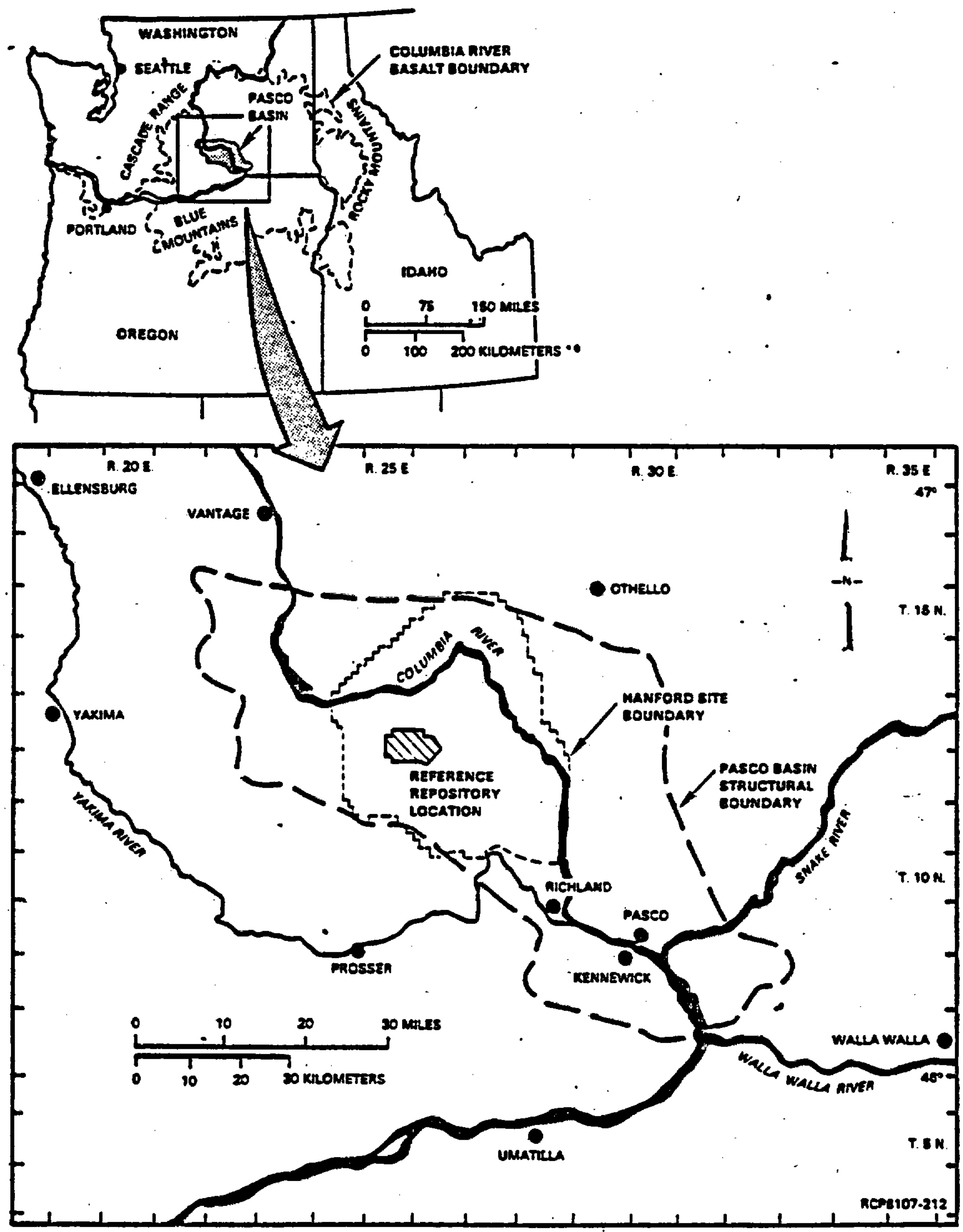


FIGURE 1-1. Location Map Showing the Hanford Site Boundary and the Reference Repository Location for a Nuclear Waste Repository in Basalt.

TABLE 1-1. Basalt Waste Isolation Project Work Breakdown Structure for Waste Package Development.

End Function	Activity	Subactivity	WBS No.
Waste Package	Waste Package Baseline	Waste Package Baseline	L211
		Waste Package Institutional Interactions	L215
	Waste Form	Acquisition of Waste Forms and Waste Form Data	L221
	Barrier Materials	Waste/Barrier/Rock Interactions	L232
		Near-Field Geochemistry	L233
		Containment Materials Testing	L234
		Packing Materials Testing	L235
	Design and Development*	Design and Engineering	L241
		Development Testing	L242
	Performance Evaluation*	Near-Field Performance Evaluation	L251
		Design Analysis	L252
		Field and In Situ Testing	L253

*Corresponding subactivities to be included in revised draft of Barrier Materials Test Plan (Section 5.0), due September 1984.

development plans shown as a hierarchy of plans in Figure 1-2 are those the BWIP has identified as required to guide the activities of the Engineered Barriers Department.* The scope of these test plans when completed or revised will be to achieve the overall objectives of the department; i.e., to develop waste package and repository seal designs which will provide reasonable assurance that the U.S. Nuclear Regulatory Commission (NRC) performance objectives will be met.

1.2 PURPOSE OF THE BARRIER MATERIALS TEST PLAN

The purpose of the BMTP is to define a waste package materials testing program that will (1) provide management control, (2) receive peer acceptance, (3) provide public information, and (4) provide sufficient information to allow the NRC staff to determine that the appropriate types and amounts of testing and analyses are planned that will meet repository licensing requirements. The BMTP will:

- Provide traceability of planned tests from the NRC numerical performance objectives (NRC, 1983a), to the issues, work requirements, and data needs
- Define the scope of the BWIP waste package materials near-field geochemistry testing
- Identify the needs and the justification for developing additional test data
- Provide the status of current testing and analyses activities
- Describe the tests and analyses to be used to provide the additional data
- Provide test control, i.e., test procedures, safety assessment, test program environment definition, quality assurance requirements, program organization, schedule, and reporting.

*A hierarchy of BWIP plans is being developed by the BWIP and when completed and approved will be included in the Engineered Barriers Test Plan to show the relationship between the Engineered Barriers test programs and the BWIP overall testing programs.

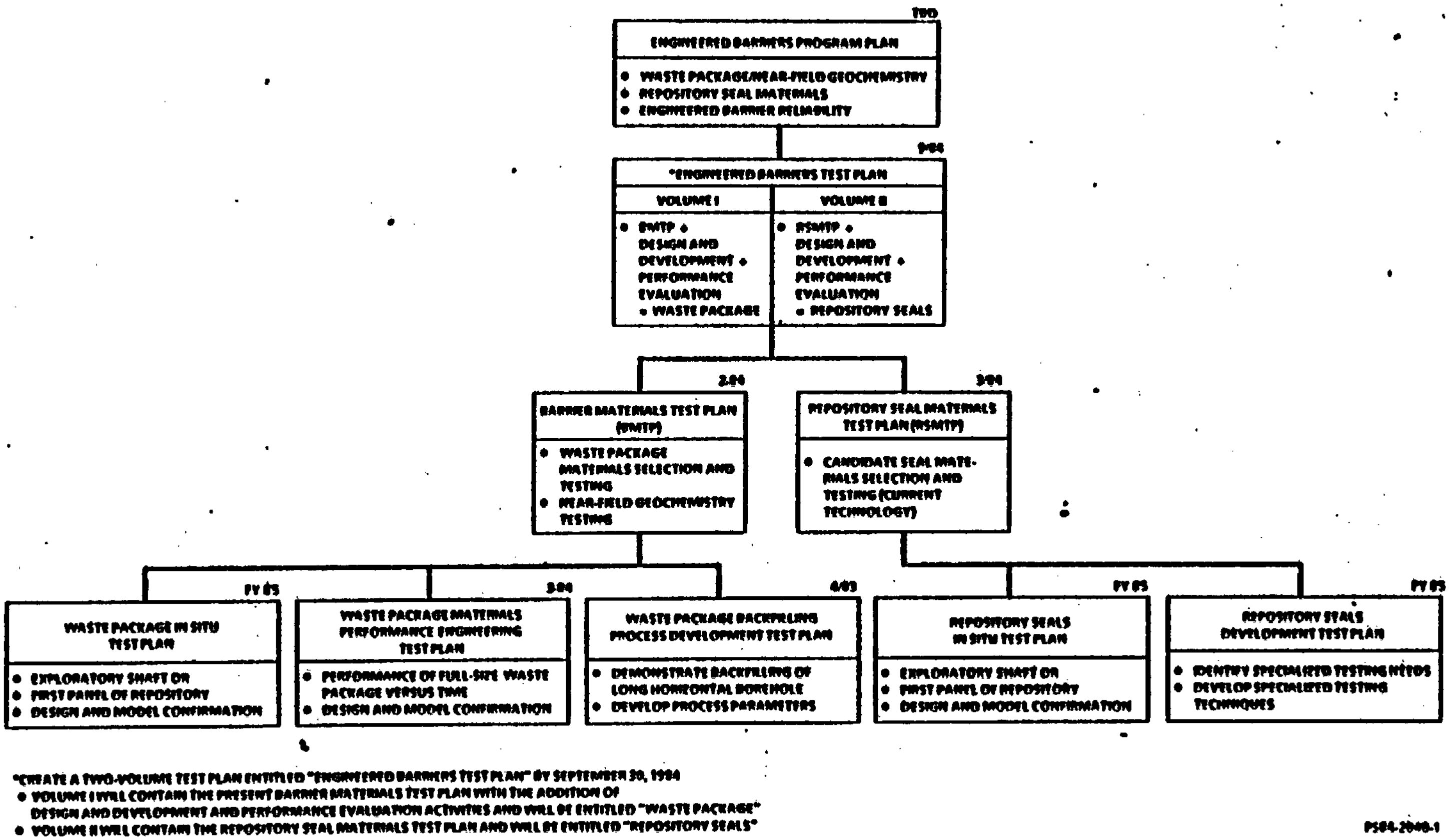


FIGURE 1-2. Program Plan and Test Plans required to Meet Waste Package and Repository Seals Performance Objectives.

2.0 OBJECTIVES

The overall objectives of the BWIP barrier materials testing program is to provide necessary data and analyses for (1) developing waste package designs and (2) quantitatively evaluating component and waste package behavior relative to the numerical performance objectives allocated from the NRC (1983a) using reliability analysis. Principal portions of these performance objectives that are related to the engineered barrier system are applicable to the two repository periods listed below.

1. During the repository operations period, two performance objectives apply:

   - 10 CFR 60.111(a), limiting radiation exposure and release to unrestricted areas of the repository (underground facility) to that specified in 10 CFR 20

   - 10 CFR 60.111(b), preserving the option of waste retrievals throughout the operations period.

2. After permanent closure, three performance objectives apply:

   - 10 CFR 60.112, limiting release of radionuclides to the accessible environment to those permitted by the U.S. Environmental Protection Agency (EPA) standard (proposed 40 CFR 191)

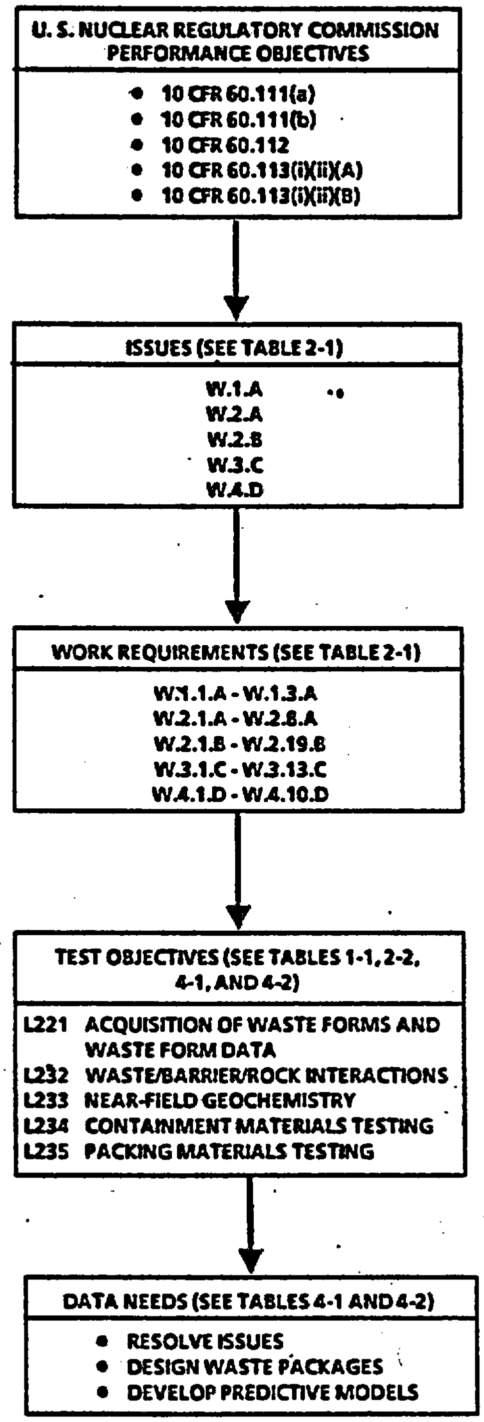
   - 10 CFR 60.113(1)(1)(ii)(A), requiring a minimum waste package containment time from 300 to 1,000 yr after permanent closure of repository

   - 10 CFR 60.113(a)(1)(ii)(B), limiting the radionuclide release rate from the engineered barrier system to one part in 100,000 per year of the inventory remaining at the end of 1,000 yr after permanent closure of repository.

These performance objectives form the basis for the identification of a sequence of events that culminate in the development of data needs and testing requirements for the resolution of issues, design of waste packages, and development of predictive models for performance assessment and design verification. This sequence is shown in Figure 2-1 where issues are defined and work requirements needed to resolve the issues are identified. The work requirements are related to appropriate subactivities of the BWIP waste package work breakdown structure (WBS) where the work will be accomplished. A test objective is stated for each subactivity and data needs are identified to satisfy the test objectives. This sequence of events is defined in more detail in Tables 2-1 and 2-2 and in Tables 4-1 and 4-2 of Section 4.0.

Table 2-1 shows the correlation of the NRC performance objectives with the waste package performance issues and the work requirements (materials testing) needed to resolve the issues. Note that there are no performance objectives associated with the waste form issue shown in Table 2-1. The issue and resulting work requirements relate to the preparation and acquisition of adequate waste forms from sources external to the BWIP and are not performance oriented. The work requirements listed under Barrier Materials (L23) are broken into two groups. The work requirements designated by "A" are related to testing of waste forms; those designated by "B" are concerned with hydrothermal testing of the waste package.

The relationship among WBS subactivities, test objectives, and work requirements is shown in Table 2-2. This same approach is used in Table 4-1, Section 4.0, to show the relationship among test objectives, work requirements, and data needs. Thus, the sets of tables in Sections 2.0 and 4.0 serve to relate waste package issues, data needs, and test objectives and to provide traceability of data to the NRC performance objectives with which the waste package must comply to meet repository licensing requirements. (Note that the issues, work requirements, and test objectives related to activity L24, Design and Development and Activity L25, Performance Evaluation are referred to in Figure 2-1 and stated in Tables 2-1, 2-2, 4-1 and 4-2, while the description of these activities are not included in Section 5.0 of this draft. They will be added in the revised draft of the BMTP due September 1984.)



PS84-2040-2

FIGURE 2-1. Data Traceability.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 1 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
W.1 Waste Form (L22)		
	W.1.A (Primary)* Considering the performance allocation assigned to the waste package, can a radionuclide release rate limit be set that will meet the waste package NRC numerical performance objectives and can a part of the performance allocation be assigned to the waste form? W.1.A (Secondary)* Can fully radioactive waste forms be prepared and adequately characterized to meet the needs of the Barrier Materials Test program?	W.1.1.A Define composition requirements and follow preparation and pretest characterization activities for defense and commercial borosilicate glass waste form needed for BWIP hydrothermal testing. W.1.2.A Acquire commercial and defense borosilicate glass waste forms and light water reactor spent fuels compositions needed for waste/barrier/rock interaction testing. W.1.3.A Develop waste acceptance requirements/specifications for a nuclear waste repository in basalt. W.1.4.A Determine the need and, if justified, acquire altered waste forms for testing.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 2 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.2 Barrier Materials (L23)	
10 CFR 60.112 limits the release of radionuclides to the accessible environment to those permitted by the EPA standard (proposed 40 CFR 191). 10 CFR 60.113(a)(1)(ii)(A) requires a minimum waste package containment time from 300 to 1,000 yr. 10 CFR 60.113(a)(1)(ii)(B) limits the radionuclide release rate from the engineered barrier system to 1 part in 100,000 per year of the inventory remaining at the end of 1,000 yr following permanent closure.	W.2.A Considering the performance allocation assigned to the waste package, can a radionuclide release rate limit be set that will meet the waste package NRC numerical performance objectives and can a part of the performance allocation be assigned to the waste form if necessary?	W.2.1.A Determine effect of borosilicate glass waste form compositions on radionuclide release rates. W.2.2.A Determine the effect of temperature, repository water compositions, pH, Eh, and flow rates on the radionuclide release rates from borosilicate glass and spent fuel waste forms. W.2.3.A Determine the effect of waste form aging on radionuclide release rate. W.2.4.A Determine the maximum operating temperature limits for waste forms, packing materials, container, and host rock.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 3 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.2 Barrier Materials (L23)	
		W.2.5.A Determine the waste package containment time and radionuclide release rate necessary to assure releases from the underground facility are within the NRC numerical performance objectives. W.2.6.A Identify and determine the properties of waste forms that change with time and that may impact the ability of the engineered barrier system to meet NRC performance objectives. W.2.7.A Determine effect of water residence time on radionuclide release from the waste form. W.2.8.A Determine effect of waste package component reaction products on release rate of radionuclides from the waste form.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 4 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.2 Barrier Materials (L23)	
10 CFR 60.112 limits the release of radionuclides to the accessible environment to those permitted by the EPA standard (proposed 40 CFR 191). 10 CFR 60.113(a)(1)(ii)(A) requires a minimum waste package containment time from 300 to 1,000 yr. 10 CFR 60.113(a)(1)(ii)(B) limits the radionuclide release rate from the engineered barrier system to 1 part in 100,000 per year of the inventory remaining at the end of 1,000 yr following permanent closure.	W.2.B Considering the performance allocation assigned to the waste package, can container and packing materials be identified that will achieve the waste package NRC performance objectives?	W.2.1.B Determine the effect of waste package materials (e.g., container corrosion product and packing materials alteration) on the groundwater composition in the presence and absence of basalt in an alpha and gamma radiation field. W.2.2.B Determine effect of changing repository environment with time on waste package component materials compatibility. W.2.3.B Determine effects of packing material, radiation, repository water composition, and temperature on the corrosion and mechanical behavior of container materials.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 5 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.2 Barrier Materials (L23)	
		W.2.4.B Determine the rate that Eh, pH, and temperature conditions in the packing material/repository water return to "ambient" conditions after repository sealing. W.2.5.B Determine the hydrothermal reactions that will occur in the waste package, groundwater, and room backfill with temperature, time, and radiation. W.2.6.B Determine what natural analogs of waste package components can be used to verify and predict the compatibility of the waste package with the repository environment.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 6 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
W.2 Barrier Materials (L23)		
		W.2.7.B Determine what part solubility, sorption, and colloid and particulate formation play in the transport of radionuclides through the packing material and repository backfill with and without alpha and gamma radiation. W.2.8.B Determine when and how water contacts the repository backfill, waste package packing material, container, and waste form. W.2.9.B Determine the effect of radiation on the physical, mechanical, and chemical properties of waste package packing material. W.2.10.B Determine the effectiveness of the packing material in restricting the flow of water to and around the container.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 7 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
W.2 Barrier Materials (L23)		
		W.2.11.B Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill. W.2.12.B Determine what waste package containment time and radionuclide release rates are necessary to assure the releases from the underground facility are within the NRC numerical performance objectives. W.2.13.B Determine what changes and to what extent chemical, physical, and mechanical properties of waste package materials will change with time under hydrothermal conditions and how these changes will affect waste package performance.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 8 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
W.2 Barrier Materials (L23)		
		W.2.14.B Determine to what extent weathered or altered basalt affect radionuclide release and retardation.
		W.2.15.B Determine if the geochemical and hydrologic properties of the engineered barrier system will permit the NRC performance objectives to be met.
		W.2.16.B Determine effects of packing materials on the corrosion mechanisms for the container in presence and absence of radiation.
		W.2.17.B Determine how Eh, pH, and PO_2 change with time in the vicinity of the container and packing material.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives; Waste Package Issues, and Work Requirements. (Sheet 9 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.2 Barrier Materials (L23)	
		W.2.18.B Determine the effects of gamma and alpha radiation on groundwater, basalt plus groundwater, and radionuclide release and retardation mechanisms. W.2.19.B Develop techniques for in situ measurement of Eh and pH.
	W.3 Design and Development (L24)	
10 CFR 60.111(a) limits radiation exposure and release to unrestricted areas of the repository to that specified in 10 CFR 20. 10 CFR 60.111(b) preserves the option of waste retrieval throughout the operations period.	W.3.C Can waste packages be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the environment do not compromise the function of the waste packages or the performance of the underground facility and geologic setting and, in addition, preserve the retrievability option?	W.3.1.C Determine what factors of safety and waste package component reliability are necessary to achieve the NRC performance objectives. W.3.2.C Design waste package so that accidental release of radionuclides to unrestricted areas are within the limits specified in 10 CFR 20.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 10 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.3 Design and Development (L24)	
10 CFR 60.112 limits the release of radionuclides to the accessible environment to those permitted by the EPA standard (proposed 40 CFR 191).		W.3.3.C Design the waste packages so that they may be retrieved at any time during the operating period if necessary.
10 CFR 60.113(i)(ii)(A) requires a minimum waste package containment time from 300 to 1,000 yr.		W.3.4.C Develop field, engineering, and in situ test plans needed to meet design and performance modeling and conduct tests.
10 CFR 60.113(i)(ii)(B) limits the radionuclide release rate from the engineered barrier system to 1 part in 100,000 per year of the inventory remaining at the end of 1,000 yr following permanent closure.		W.3.5.C Determine the mechanical loads on a waste package container as a function of time during handling, transporting, and emplacing and during unforeseen events after emplacement.
		W.3.6.C Determine the design and reliability requirements for waste packages and components for emplacement in a nuclear waste repository in basalt.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 11 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
W.3 Design and Development (L24)		
		W.3.7.C Determine development needs and conduct welding and non-destructive examination methods for the waste container. W.3.8.C Demonstrate remote welding and non-destructive examination of the closure welds on a waste package container. W.3.9.C Conduct tests and engineering studies necessary to provide data for the preparation of waste package design requirements. W.3.10.C Determine conditions that might affect criticality and evaluate criticality potential within and between waste packages.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 12 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.3 Design and Development (L24)	
		W.3.11.C Complete engineering analysis of failure modes for life history of the waste package and estimate these contributions towards failure. W.3.12.C Complete waste package advanced conceptual design requirements and designs for commercial, defense, and spent fuel waste forms. W.3.13.C Prepare waste package preliminary and final design requirements to complete designs for commercial, defense, and spent fuel waste forms.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 13 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.4 Performance Evaluation (L25)	
10 CFR 60.112 limits the release of radionuclides to the accessible environment to those permitted by the EPA standard (proposed 40 CFR 191). 10 CFR 60.113(a)(1)(ii)(A) requires a minimum waste package containment time from 300 to 1,000 yr. 10 CFR 60.113(a)(1)(ii)(B) limits the radionuclide release rate from the engineered barrier system to 1 part in 100,000 per year of the inventory remaining at the end of 1,000 yr following permanent closure.	W.4.D Can a performance model be developed and validated that will reliably predict waste package performance for the time periods required by the NRC performance objectives?	W.4.1.D Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill. W.4.2.D Determine when and how the water contacts the repository backfill, waste package packing material, container, and waste form. W.4.3.D Develop a quantitative waste package reliability plan and procedures to demonstrate the reliability of designs and determine importance of specific uncertainties in system performance.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 14 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.4 Performance Evaluation (L25)	
		W.4.4.D Identify and develop test plans needed for measuring the behavior of full sized waste packages under conditions that simulate as closely as possible those existing in a nuclear waste repository in basalt. Conduct the tests to meet program schedules. W.4.5.D Develop in situ test plans for monitoring waste packages in a suitable below-grade test facility. W.4.6.D Develop and validate a waste package degradation model to describe failure modes of container and packing material. W.4.7.D Develop and validate radionuclide transport model for the waste package.

TABLE 2-1. Relationship Among U.S. Nuclear Regulatory Commission Performance Objectives, Waste Package Issues, and Work Requirements. (Sheet 15 of 15)

U.S. Nuclear Regulatory Commission performance objectives	Issue	Work requirements
	W.4 Performance Evaluation (L25)	
		W.4.8.D Determine effect of temperature and stress on the host basalt. W.4.9.D Predict changes in chemical environment surrounding the waste package with time.

Note: BWIP = Basalt Waste Isolation Project.
EPA = U.S. Environmental Protection Agency.
NRC = U.S. Nuclear Regulatory Commission.

*Primary and secondary issues were identified for Activity W.1, Waste Form, since it provides support to Activity W.2, Barrier Materials; the primary issue will be resolved through testing.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 1 of 16)

Work breakdown structure	Test objectives	Work requirements
	Waste Form (L22)	
(L221) Acquisition of Waste Forms and Waste Form Data	Acquire waste forms for the waste/barrier/rock hydrothermal testing and provide an adequate data base on chemical and physical properties of waste forms.	W.1.1.A Define compositional requirements and follow preparation and pre-test characterization activities for defense and commercial borosilicate glass waste form needed for BWIP hydrothermal testing. W.1.2.A Acquire commercial and defense borosilicate glass waste forms and light water reactor spent fuels compositions needed for waste/barrier/rock interaction testing. W.1.3.A Develop waste acceptance requirements/specifications for a nuclear waste repository in basalt. W.1.4.A Determine the need and, if justified, acquire altered waste forms for testing.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 2 of 16)

Work breakdown structure	Test objectives	Work requirements
Barrier Materials (L23)		
(L232) Waste/Barrier/Rock Interactions	Provide sufficient data on chemical interactions among waste package components and host rock exposed to the environment of a nuclear waste repository in basalt to assess radionuclide release rates from the waste package and its ability to meet NRC performance objectives.	W.2.1.A Determine effect of borosilicate glass waste form compositions on radionuclide release rates.
		W.2.2.A Determine the effect of temperature, repository water composition, pH, Eh, and flow rates on the radionuclide release rates from borosilicate glass and spent fuel waste forms.
		W.2.3.A Determine the effect of waste form aging on radionuclide release rate.
		W.2.4.A Determine the maximum operating temperature limits for waste forms, packing materials, container, and host rock.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 3 of 16)

Work breakdown structure	Test objectives	Work requirements
	Barrier Materials (L23)	
		W.2.5.A Determine the waste package containment time and radionuclide release rate necessary to assure releases from the underground facility are within the NRC numerical performance objectives.
		W.2.6.A Identify and determine the properties of waste forms that change with time and that may impact the ability of the engineered barrier system to meet NRC performance objectives.
		W.2.7.A Determine effect of water residence time on radionuclide release from the waste form.
		W.2.8.A Determine effect of waste package component reaction products on release rate of radionuclides from the waste form.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 4 of 16)

Work breakdown structure	Test objectives	Work requirements
Barrier Materials (L23)		
		W.2.1.B Determine the effect of waste package materials (e.g., container corrosion product and packing materials alteration) on the groundwater composition in the presence and absence of basalt in an alpha and gamma radiation field. W.2.2.B Determine effect of changing repository environment with time on waste package component materials compatibility. W.2.4.B Determine the rate that Eh, pH, and temperature conditions in the packing material/repository water return to "ambient" conditions after repository sealing. W.2.5.B Determine the hydrothermal reactions that will occur in the waste package, groundwater, and room backfill with temperature, time, and radiation.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 5 of 16)

Work breakdown structure	Test objectives	Work requirements
Barrier Materials (L23)		
		W.2.11.B Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill. W.2.13.B Determine what changes and to what extent chemical, physical, and mechanical properties of waste package materials will change with time under hydrothermal conditions and how these changes affect waste package performance. W.2.14.B Determine to what extent weathered or altered basalt affects radionuclide release and retardation. W.2.15.B Determine if the geochemical and hydrologic properties of the engineered barrier system will permit the NRC performance objectives to be met.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 6 of 16)

Work breakdown structure	Test objectives	Work requirements
Barrier Materials (L23)		
		W.2.17.B Determine how Eh, pH, and PO_2 change with time in the vicinity of the container and packing material. W.2.18.B Determine the effects of gamma and alpha radiation on groundwater, basalt plus groundwater, and radionuclide release and retardation mechanisms. W.2.19.B Develop techniques for in situ measurement of Eh and pH.
(L233) Near-Field Geochemistry	Provide sufficient data on radionuclide solubility, sorption, and colloid formation to allow reliable prediction of radionuclide release and transport in the waste package and the repository horizon.	W.2.6.B Determine what natural analogs of waste package components can be used to verify and predict the compatibility of the waste package with the repository environment.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 7 of 16)

Work breakdown structure	Test objectives	Work requirements
Barrier Materials (L23)		
		W.2.7.B Determine what part solubility, sorption, and colloid and particulate formation play in the transport of radionuclides through the packing material and repository backfill with and without alpha and gamma radiation. W.2.11.B Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill. W.2.18.B Determine the effects of gamma and alpha radiation on groundwater, basalt plus groundwater, and radionuclide release and retardation mechanisms.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 8 of 16)

Work breakdown structure	Test objectives	Work requirements
Barrier Materials (L23)		
(L234) Containment Materials Testing	Provide sufficient data on the reference and backup containment materials exposed to the simulated environment of a nuclear waste repository in basalt to assess their ability to meet design and reliability requirements and NRC performance objectives.	W.2.3.B Determine effects of packing material, radiation, repository water composition, and temperature on the corrosion and mechanical behavior of container materials. W.2.8.B Determine when and how water contacts the repository backfill, waste package packing material, container, and waste form. W.2.16.B Determine effects of packing materials on the corrosion mechanisms for the container in presence and absence of radiation.
(L235) Packing Materials Testing	Provide sufficient data on the candidate packing materials exposed to the simulated environment of a nuclear waste repository in basalt to assess their ability to meet design and reliability requirements and NRC performance objectives.	W.2.4.B Determine the rate that Eh, pH, and temperature conditions in the packing material/repository water return to "ambient" conditions after repository sealing.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 9 of 16)

Work breakdown structure	Test objectives	Work requirements
	Barrier Materials (L23)	
		W.2.8.B Determine when and how water contacts the repository backfill, waste package packing material, container, and waste form. W.2.9.B Determine the effect of radiation on the physical, mechanical, and chemical properties of waste package packing material. W.2.10.B Determine the effectiveness of the packing material in restricting the flow of water to and around the container.
	Design and Development (L24)	
(L241) Design and Engineering	Conduct engineering studies and develop requirements for the design of reliable waste packages for a nuclear waste repository in basalt that will meet the NRC peformance objectives.	W.3.1.C Determine what factors of safety and waste package component reliability are necessary to achieve the NRC performance objectives.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 10 of 16)

Work breakdown structure	Test objectives	Work requirements
Design and Development (L24)		
		W.3.2.C Design waste package so that accidental release of radionuclides to unrestricted areas are within the limits specified in 10 CFR 20. W.3.3.C Design the waste packages so that they may be retrieved at any time during the operating period if required. W.3.5.C Determine the mechanical loads on a waste package container as a function of time during handling, transporting, and emplacing and during unforeseen events after emplacement. W.3.6.C Determine the design and reliability requirements for waste packages and components for emplacement in a nuclear waste repository in basalt.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 11 of 16)

Work breakdown structure	Test objectives	Work requirements
Design and Development (L24)		
		W.3.10.C Determine conditions that might affect criticality and evaluate criticality potential within and between waste packages. W.3.11.C Complete engineering analysis of failure modes for life history of the waste package and estimate these contributions toward failure. W.3.12.C Complete waste package advanced conceptual design requirements and designs for commercial, defense, and spent fuel waste forms. W.3.13.C Prepare waste package preliminary and final design requirements to complete designs for commercial, defense, and spent fuel waste forms.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 12 of 16)

Work breakdown structure	Test objectives	Work requirements
	Design and Development (L24)	
(L242) Development Testing	Conduct design development testing leading to the selection of final designs for reliable waste packages for commercial and defense high-level wastes and spent fuel for a nuclear waste repository in basalt that will meet the NRC performance objectives.	W.3.4.C Develop field, engineering, and in situ test plans needed to meet design and performance modeling and conduct tests. W.3.7.C Determine development needs and conduct welding and non-destructive examination methods for the waste container. W.3.8.C Demonstrate remote welding and non-destructive examination of the closure welds on a waste package container. W.3.9.C Conduct tests and engineering studies necessary to provide data for the preparation of waste package design requirements.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 13 of 16)

Work breakdown structure	Test objectives	Work requirements
	Performance Evaluation (L25)	
(L251) Near-Field Performance Evaluation	Develop models to define radionuclide release from the waste form and behavior in the waste package and geochemical environment of a nuclear waste repository in basalt.	W.2.8.B Determine when and how water contacts the repository backfill, waste package packing material, container, and waste form. W.2.11.B Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill. W.2.12.B Determine what waste package containment time and radionuclide release rates are necessary to assure the releases from the underground facility are within the NRC numerical performance objectives. W.2.16.B Determine effects of packing materials on the corrosion mechanisms for the container in presence and absence of radiation.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 14 of 16)

Work breakdown structure	Test objectives	Work requirements
	Performance Evaluation (L25)	
		W.4.1.D Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill. W.4.7.D Develop and validate radionuclide transport model for the waste package. W.4.9.D Predict changes in chemical environment surrounding the waste package with time.
(L252) Design Analysis	Develop models to predict waste package performance and provide reliability requirements for waste packages sufficient to meet the NRC performance objectives.	W.2.10.B Determine the effectiveness of the packing material in restricting the flow of water to and around the container.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 15 of 16)

Work breakdown structure	Test objectives	Work requirements
Performance Evaluation (L25)		
		W.2.4.A Determine the maximum operating temperature limits for waste forms, packing materials, container, and host rock. W.3.6.C Determine the design and reliability requirements for waste packages and components for emplacement in a nuclear waste repository in basalt. W.4.2.D Determine when and how the water contacts the repository backfill, waste package packing material, container, and waste form. W.4.3.D Develop a quantitative waste package reliability plan and procedures to demonstrate the reliability of designs and determine importance of specific uncertainties in system performance.

TABLE 2-2. Relationship Among Waste Package Work Breakdown Structure, Waste Package and Near-Field Geochemistry Test Objectives, and Work Requirements. (Sheet 16 of 16)

Work breakdown structure	Test objectives	Work requirements
	Performance Evaluation (L25)	
		W.4.6.D Develop and validate a waste package degradation model to describe failure modes of container and packing material. W.4.8.D Determine effect of temperature and stress on the host basalt.
(L253) Field and In Situ Testing	Provide sufficient data from field/engineering testing and in situ monitoring to confirm waste package design and performance predictions.	W.4.4.D Identify and develop test plans needed for measuring the behavior of full sized waste packages under conditions that simulate as closely as possible those existing in a nuclear waste repository in basalt. Conduct the tests to meet program schedules. W.4.5.D Develop in situ test plans for monitoring waste packages in a suitable below-grade test facility.

Note: BWIP = Basalt Waste Isolation Project.
NRC = U.S. Nuclear Regulatory Commission.

3.0 SCOPE

The scope of the BMTP includes the materials testing and data collection necessary for the preparation of waste package design requirements and design development as well as the data required (including near-field geochemistry: sorption, solubility, etc.) for waste package performance modeling and model verification and validation. The test plan provides justification (Section 4.0) for the testing needed to develop an adequate data base to support these activities. The status of testing and analyses and the additional data and analyses presently judged to be required to complete the waste package data base are documented in Section 5.0.

The data needs described in the BMTP were established from:

- The BWIP present understanding of what will be needed to meet the NRC numerical performance objectives (NRC, 1983a) which were established from regulatory requirements

- A review of the data needs identified in the NRC Draft Site Characterization Analyses (NRC, 1983b)

- A review of the NRC Technical Position, Subtask 1.1: Waste Package Performance of the Repository Closure (NRC, 1983c)

- Other documentation resulting from reviews of the BWIP Site Characterization Report (DOE-RL, 1982).

By June 1, 1984, a quantitative reliability program plan and procedures will be developed. The use of the procedures will aid in determining test plan completeness by defining with "reasonable assurance" when the data base is adequate to meet waste package design and performance model development needs. Thus, with the use of reliability analysis, two key questions may be answered: what data are needed and when has enough testing been completed.

A complex activity such as the BMTP requires a systematic approach to planning and control of the program. Such an approach proceeds stepwise from a definition of program requirements, information needs and objectives through testing, and documentation of results as shown in Figure 3-1. The Engineered Barriers Department is following this approach to ensure that the data to be developed from the BMTP will meet repository licensing requirements. To assure that data are valid for licensing purposes, the BWIP Quality Assurance Group will be involved in each step of the program as shown in Figure 3-1. This approach also assures timely access to data by the NRC for their assessment.

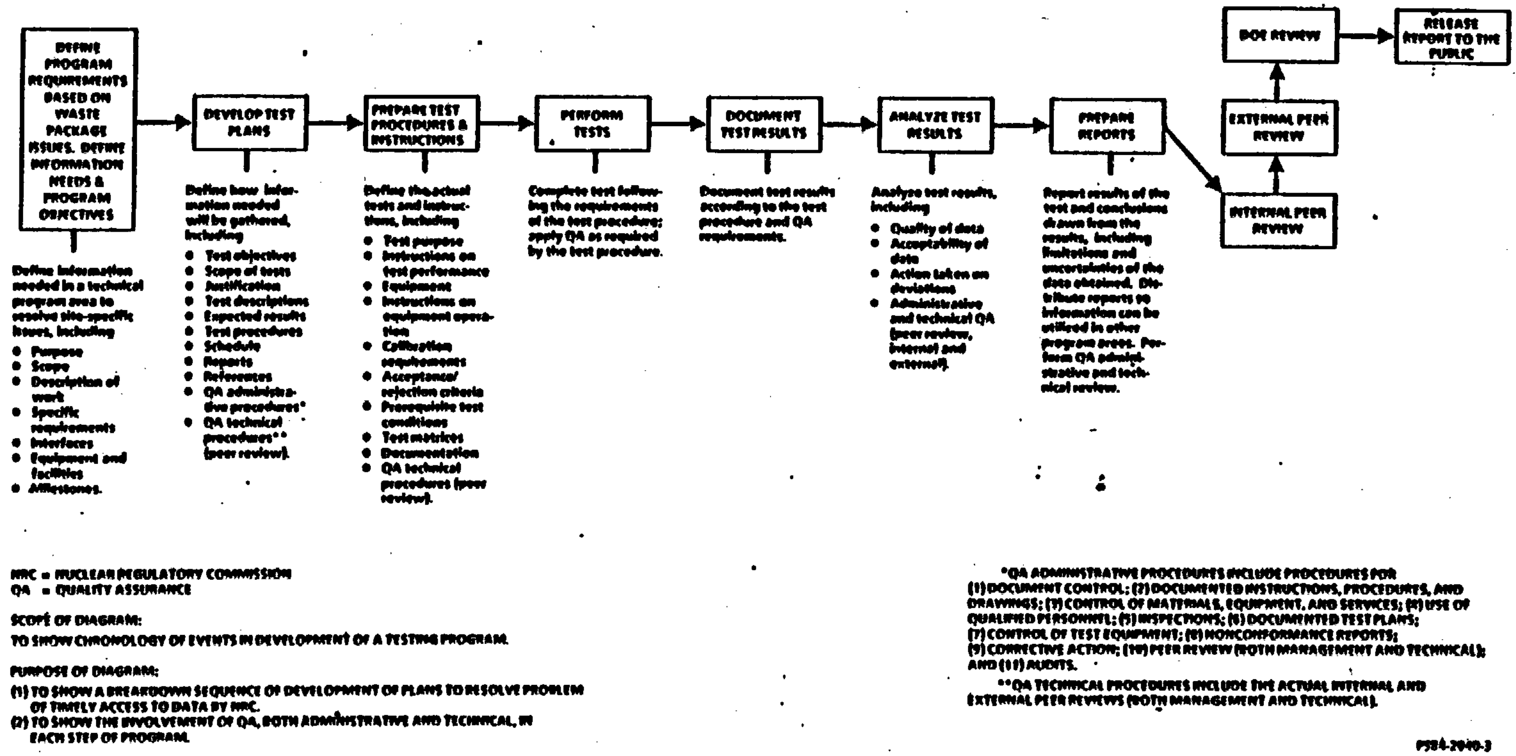


FIGURE 3-1. Technical Program Control--Test Plans and Procedures.

3.1 WASTE PACKAGE AND REPOSITORY SEALS TEST PLANS

The BMTP is one of several test plans (see Fig. 1-2) to be developed to guide the design, testing, and performance modeling activities within the Engineered Barriers Department. The test plans fall within the bounds defined by an engineered barrier program plan which will be prepared from appropriate parts of Chapter 11 of the Site Characterization Plan. The test plans are summarized or justified as follows.

3.1.1 Waste Package In Situ Test Plan

A preliminary Waste Package In Situ Test Plan will be completed during FY 1984 leading to the fulfillment of the requirements of 10 CFR 60.140 and 60.143 (NRC, 1983a) which state in part:

"(a) The performance confirmation program shall provide data which indicates, where practicable, whether--

(1) Actual subsurface conditions encountered and changes in those conditions during construction and waste emplacement operations are within the limits assumed in the licensing review; and

(2) Natural and engineered systems and components required for repository operation, or which are designed or assumed to operate as barriers after permanent closure, are functioning as intended and anticipated.

(b) The program shall have been started during site characterization and it will continue until permanent closure.

(c) The program shall include in situ monitoring, laboratory and field testing, and in situ experiments, as may be appropriate to accomplish the objective as stated above."

and

"(a) A program shall be established at the geologic repository operations area for monitoring the condition of the waste packages. Waste packages chosen for the program shall be representative of those to be emplaced in the underground facility.

(b) Consistent with safe operation at the geologic repository operations area, the environment of the waste packages selected for the waste package monitoring program shall be representative of the environment in which the wastes are to be emplaced.

(c) The waste package monitoring program shall include laboratory experiments which focus on the internal condition of the waste packages within the underground facility during the waste package monitoring program shall be duplicated in the laboratory experiments.

(d). The waste package monitoring program shall continue as long as practical up to the time of permanent closure."

The in situ testing or monitoring of waste packages will be conducted during the second phase of the exploratory shaft test program and/or in the first waste panel of the repository and continue until repository closure.

3.1.2 Repository Seals In Situ Test Plan

A Repository Seals In Situ Test Plan will be completed during FY 1985 leading to the fulfillment of the requirements of 10 CFR 60.142 (NRC, 1983a) which state:

"(a) During the early or developmental stages of construction, a program for in situ testing of such features as borehole and shaft seals, backfill, and the thermal interaction effects of waste packages, backfill, rock, and groundwater shall be conducted.

(b) The testing shall be initiated as early as practicable.

(c) A backfill test section shall be constructed to test the effectiveness of backfill placement and compaction procedures against design requirements before permanent backfill placement is begun.

(d) Test sections shall be established to test the effectiveness of borehole and shaft seals before full-scale operation proceeds to seal boreholes and shafts."

The in situ testing or monitoring will be conducted during the second phase of the exploratory shaft test program and/or in the first waste panel of the repository and continue until repository closure.

3.1.3 Waste Package Materials Performance Engineering Test Plan

The Waste Package Materials Performance Engineering Test Plan covers a testing program utilizing full-scale waste packages containing electric heaters to simulate radiogenic heat. The program covers essentially two separate tests. The first, which uses a pressure vessel to contain the waste package to be tested, is designed to measure the rate of ingress of water through the packing materials (75% crushed basalt and 25% bentonite) under a temperature gradient for design and predictive model confirmation. The test will be initiated on October 1986 and terminated in time for post-test materials evaluation and data input to the Site Recommendation Report in January 1990 and to the License Application in November 1990.

The second test will use two pressure vessels, each to contain a full-sized waste package to measure the rate of degradation of reference waste package materials under fully saturated conditions. The objective of this test is to provide a preliminary waste package materials performance confirmation. Testing will be initiated in October 1986. The first waste package will be retrieved for evaluation and later input to the Site Recommendation Report in January 1990 and to the License Application in November 1990. The second test will continue through 1994.

3.1.4 Waste Package Backfilling Process Development Test Plan

The Waste Package Backfilling Process Development Test Plan is being conducted for the BWIP by the Westinghouse-Waste Technology Services Division. This test plan defines the program for (1) determining if basalt bentonite packing materials can be pneumatically installed into a test arrangement that is dimensionally representative of the long horizontal emplacement hole of the nuclear waste repository in basalt conceptual design, (2) defining the key parameters used, and (3) developing specifications for the packing materials, the emplacement process, and quality controls.

3.1.5 Repository Seal Materials Test Plan

The Repository Seal Materials Test Plan, to be completed in March 1984, will identify candidate repository seal materials and the testing and evaluation defined to select reference materials for long-term testing to verify their performances to meet the criteria defined in 10 CFR 60.134 (NRC, 1983a). These criteria are:

"(a) General design criterion. Seals for shafts and boreholes shall be designed so that following permanent closure they do not become pathways that compromise the geologic repository's ability to meet the performance objectives or the period following permanent closure.

(b) Selection of materials and placement methods. Materials and placement methods for seals shall be selected to reduce, to the extent practicable: (1) The potential for creating a preferential pathway for groundwater; or (2) radioactive waste migration through existing pathways."

Materials testing has been initiated and will provide data for development of seals preliminary design requirements by April 1986 and the License Application by November 1990.

3.1.6 Engineered Barriers Test Plan

After March 1984, the Barrier Materials Test Plan and the Repository Seal Materials Test Plan will be updated by September 30, 1984, to include Design and Development and Performance Evaluation and will become Volume 1 and Volume 2 of the Engineered Barriers Test Plan. This major test plan will accompany the Site Characterization Plan when it is issued to DOE on December 28, 1984.

3.1.7 Seals Development Test Plan

The Repository Seals Development Test Plan describes specialized testing required to demonstrate the performance of repository seal designs and materials. Whereas the Repository Seal Materials Test Plan defines testing using current technology, this test plan will define requirements for development of specialized equipment, instrumentation, and procedures needed to obtain the desired test results. The Repository Seal Materials Test Plan is to be completed during FY 1985. Testing will be initiated in October 1985 and will provide data to support seal designs during the course of the program and the License Application in November 1990.

3.2 TESTING BY BASALT WASTE ISOLATION PROJECT SUBCONTRACTORS

The Engineered Barriers design and materials testing program is presently scheduled to be completed by the end of fiscal year 1994 except for waste package design confirmation testing (monitoring tests) which will continue during repository construction. All materials testing is being conducted under conditions that match the environment expected in a nuclear waste repository in basalt as closely as possible. At the present time, certain tasks of the waste package testing are being conducted by the BWIP and the contractors to the BWIP, which include Westinghouse Hanford Company (WHC), the Westinghouse-Waste Technology Services Division, Temple University, and the Rockwell Science Center. The effects of radiation on container and packing materials and on groundwater are being assessed by Pacific Northwest Laboratory (PNL). In addition, PNL is studying the solubility of key radionuclide and sorption on colloids. Corrosion and mechanical testing of candidate container materials is being conducted by PNL and WHC. Temple University is conducting basalt/water interactions tests and Eh/pH probe development. Westinghouse-Waste Technology Services Division is conducting packing materials development tests and alternate waste package configuration engineering studies. Finally, the performance of actual spent fuel, radionuclide-doped and fully radioactive waste forms in the presence of waste package component materials and simulated Grande Ronde groundwater is being assessed by PNL and WHC under the direction of the BWIP using hot cell facilities located in the 325 Building, 300 Area of the Hanford Site. In addition, the Rockwell hot cell facility in the 222S laboratory in 200 West Area of the Hanford Site is being prepared for testing of radioactive waste forms plus basalt and waste package materials using a flowthrough test apparatus to be described in Subsection 5.1.2.1.5.2.

3.3 OUTLINE OF REMAINDER OF BARRIER MATERIALS TEST PLAN

As discussed previously, this edition of the BMTP is scoped to cover laboratory testing of candidate waste package component materials and near-field geochemistry (solubility, sorption, colloid formation). The next update will include Design and Development and Performance Evaluation activities. The latter activity will include the plan and procedures for assessing the reliability of waste package designs. The remainder of this test plan is outlined below. The justification for the additional data needs is provided in Section 4.0. Section 5.0 follows the waste package WBS (see Table 1-1). For each subactivity the test objective is stated, the data needs and uses and the testing techniques to be employed are tabulated, a summary of testing or analyses required to obtain the data are given, planned testing is discussed, and the subactivity description is completed with a logic network to show the planned flow of work needed to meet the test objective. The remainder of the test plan contains Test Procedures and Instructions (Section 6.0), Safety (Section 7.0), Environmental Effects (Section 8.0), Quality Assurance (Section 9.0), Organization (Section 10.0), Program Schedule and Summary Logic Network (Section 11.0), Reports (Section 12.0), and References (Section 13.0).

4.0 JUSTIFICATION

The current strategy for isolating nuclear wastes relies on a series of multiple barriers (engineered and natural) to restrict the release of radionuclides to the accessible environment. The strategy is based on a philosophy of technical conservatism that requires the use of multiple barriers to provide reasonable assurance that releases of radionuclides from the engineered barrier system do not exceed the NRC numerical performance objectives (see Section 2.0) for anticipated and unanticipated processes and events. The major subsystems of the mined geological disposal systems are the waste package and the repository (engineered barrier system) and the natural geologic medium. Of these, the waste package, consisting of multiple components, is the subsystem which can most directly influence the performance of a mined geological disposal system.

The need to provide "reasonable assurance" (NRC, 1983a) that the waste package will meet the NRC performance objectives for licensing provides the justification for the Engineered Barriers Department waste package materials testing and design program. Because of this need, a great deal of emphasis is being placed on the collection of needed data for materials selection, model development, and the development of waste packge design requirements for the BWIP architect/engineer. By careful laboratory experimentation, modeling efforts, engineering/field testing, and examination of natural and manmade artifacts (analogs), it is expected that waste packages can be designed for a nuclear waste repository in basalt that will provide reasonable assurance that they will meet the NRC performance objectives for the time periods illustrated in Figure 4-1. The alternative selected from Figure 4-1 will depend on which waste package design option is chosen.

As mentioned previously, the BWIP will develop a quantitative reliability plan to support the NRC "reasonable assurance" criterion. This plan will provide the basis for quantitatively defining the reliability of each component of the waste package. The reliability of each component is affected by the design of each and the quantity and quality of test data used. Once the reliability requirement for each component is defined, then the quality and quantity of testing associated with establishing the reliability of the waste package can be more closely defined. For the present, the data perceived as needed to meet NRC performance objectives for the waste predictive modeling and design for waste isolation in a nuclear waste repository in basalt are shown in Tables 4-1 and 4-2 together with related test objectives and work requirements. The way the data are to be utilized and the testing required to achieve the test objectives are defined in tables contained throughout Section 5.0.

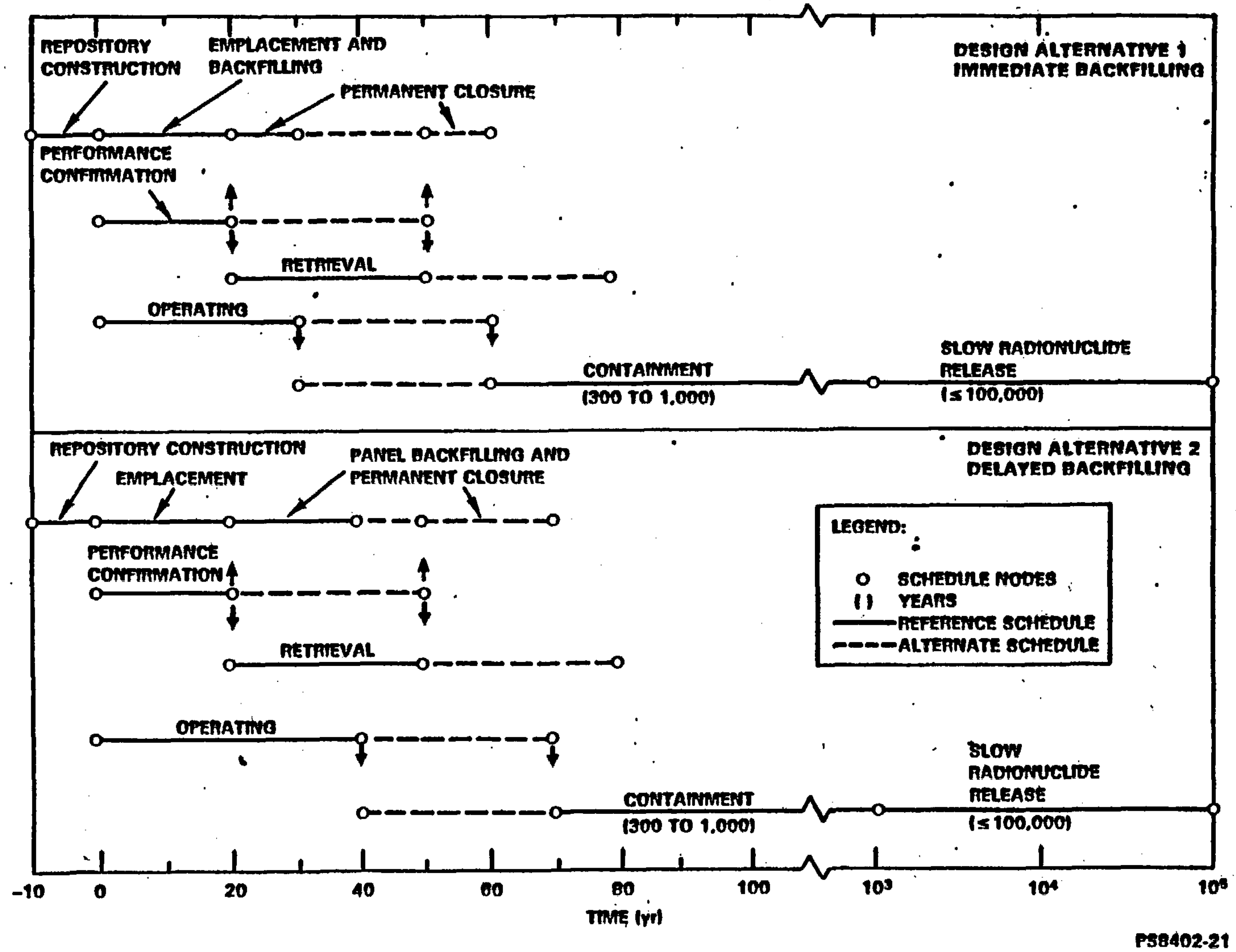


FIGURE 4-1. Repository Design Alternatives: A Schedule of Project Phases.

TABLE 4-1. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Materials and Data Needs.* (Sheet 1 of 4)

WBS	Test objectives	Work requirements	Materials and data needs
L221	Acquire waste forms for the waste/barrier/rock hydrothermal testing and provide data base on chemical and physical properties of waste form.	W.1.1.A Define composition requirements and follow preparation and pre-test characterization activities for defense and commercial borosilicate glass waste form needed for BWIP hydrothermal testing. W.1.2.A Acquire commercial and defense borosilicate glass waste forms and light water reactor spent fuels compositions needed for waste/barrier/rock interaction testing. W.1.3.A Develop waste acceptance requirements/specifications for a nuclear waste repository in basalt. W.1.4.A Determine the need and, if justified, acquire altered waste forms for testing.	<u>LWR Spent Fuels</u> Simulated LWR spent fuel (nonradioactive dopants) for subcontractor (Arizona State University) testing PWR and BWR spent fuels of normal and off-normal history (design, fabrication, and irradiation) Turkey Point reactor PWR (normal) available 9/30/83 H. B. Robinson II reactor PWR (ATM-101) (normal) available 1/31/84 <u>CHLW (Waste Forms)</u> PNL 76-68 borosilicate glass loaded with a nonradioactive simulation of a CHLW for subcontractor (Arizona State University) testing Tracer-doped PNL 77-260 borosilicate glass - the early reference glass for Barnwell CHLW (Slate et al., 1981) (^{238}U, ^{239}Pu, ^{237}Np, ^{241}Am, and ^{99}Tc), available 9/30/82

TABLE 4-1. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Materials and Data Needs.* (Sheet 2 of 4)

WBS	Test objectives	Work requirements	Materials and data needs
			Tracer-doped PNL 76-68 borosilicate glass (^{238}U and ^{99}Tc), available 12/30/82
			Tracer-doped PNL 76-68 borosilicate glass (^{238}U, ^{239}Pu, and ^{237}Np), available 12/31/82
			High-level doped BWIP Glass A (ATM-6) (PNL Interim Barnwell Process glass, i.e. replacement for PNL 77-260) (^{238}U, ^{239}Pu, ^{240}Pu, ^{237}Np, ^{244}Cm, ^{99}Tc, ^{137}Cs, and ^{75}Se), available 9/30/83
			High-level doped BWIP Glass B (^{238}U, ^{241}Am, ^{226}Ra, ^{232}Th, ^{113}Sn, and ^{75}Se), available 3/31/84
			Actual spent fuel, waste fully loaded into PNL 76-68 borosilicate glass (ATM-5), available 4/31/83
			High-level doped West Valley Vitrification Project reference borosilicate glass waste form (dopants to be determined), available 12/31/85

TABLE 4-1. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Materials and Data Needs.* (Sheet 3 of 4)

WBS	Test objectives	Work requirements	Materials and data needs
			DHLW (Waste Forms) Simulated Savannah River DWPF waste form, Frit 131 with nonradioactive dopants, provided by SRL, available 6/83 High-level doped BWIP Glass D, Savannah River DWPF reference waste form, Frit 165 borosilicate glass (^{238}U, ^{239}Pu, ^{241}Am, ^{237}Np, ^{99}Tc, and ^{152}Eu), available 3/31/84 Hanford high-level doped waste form based on B Plant Immobilization Pilot Plant Project (to be determined) TRU Waste Forms Commercial TRU Waste (to be determined) Defense TRU Waste (to be determined) Waste Form Reference Data Types, sources, quantities, composition (radioactive and nonradioactive), radiation, and thermal (decay heat) inventory

TABLE 4-1. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Materials and Data Needs.* (Sheet 4 of 4)

WBS	Test objectives	Work requirements	Materials and data needs
			Waste Acceptance Requirements SD-BWI-CR-018 (Rockwell, 1983a) (draft being revised as per DOE and subcontractor reviews) FY 1986 (develop preliminary specifications) FY 1988 develop final (draft) specifications

*These data needs are repeated in each subactivity of Section 5.0 where the range of test parameters and test and analytical equipment/techniques are also included.

Note: BWIP = Basalt Waste Isolation Project
BWR = Boiling water reactor
CHLW = Commercial High-Level Waste
DHLW = Defense High-Level Waste
DOE = U.S. Department of Energy
DWPF = Defense Waste Processing Facility
LWR = Light water reactor
PWR = Pressurized water reactor
SRL = Savannah River Laboratory
TRU = Transuranic
WBS = Work breakdown structure

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 1 of 14)

WBS	Test objectives	Work requirements	Data needs
L232	Provide sufficient data on chemical interactions among waste package components and host rock exposed to the environment of a nuclear waste repository in basalt to assess radionuclide release rates from the waste package and its ability to meet NRC performance objectives.	W.2.1.A Determine effect of borosilicate glass waste form compositions on radionuclide release rates. W.2.2.A Determine the effect of temperature, repository water compositions, pH, Eh, and flow rates on the radionuclide release rates from borosilicate glass and spent fuel waste forms. W.2.3.A Determine the effect of waste form aging on radionuclide release rate. W.2.4.A Determine the maximum operating temperature limits for waste forms, packing materials, container, and host rock.	1. Steady-state radionuclide concentrations in test solution 2 Steady-state cation concentrations in test solution 3. Steady-state anion concentrations in test solution 4. pH versus time 5. Eh versus time 6. Characteristics of hydrothermal alteration products 7. Altered groundwater chemical composition 8. Effects of radiation (alpha and gamma) on hydrothermal reactions and groundwater 9. Radionuclide release rate versus groundwater flow rate and residence time 10. Effect of temperature on hydrothermal stability of waste forms, container, packing material, and host rock

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 2 of 14)

WBS	Test objectives	Work requirements	Data needs
		W.2.6.A Identify and determine the properties of waste forms that change with time and that may impact the ability of the engineered barrier system to meet NRC performance objectives.	11. Physical and chemical stability of waste forms under hydrothermal conditions (static and dynamic)
		W.2.7.A Determine effect of water residence time on radionuclide release from the waste form.	12. Container material corrosion mechanisms and rates versus changing repository environment
		W.2.8.A Determine effect of waste package component reaction products on release rate of radionuclides from the waste form.	13. Packing materials stability versus changing repository environment
		W.2.1.B Determine the effect of waste package materials (e.g., container corrosion product and packing materials alteration) on the groundwater composition in the presence and absence of basalt in an alpha and gamma radiation field.	
		W.2.2.B Determine effect of changing repository environment with time on waste package component materials compatibility.	

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 3 of 14)

WBS	Test objectives	Work requirements	Data needs
		W.2.4.B Determine the rate that Eh, Ph, and temperature conditions in the packing material/repository water return to "ambient" conditions after repository sealing.	
		W.2.5.B Determine the hydrothermal reactions that will occur in the waste package, groundwater, and room backfill with temperature, time, and radiation.	
		W.2.11.B Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill.	
		W.2.13.B Determine what changes and to what extent chemical, physical, and mechanical properties of waste package materials will change with time under hydrothermal conditions and how these changes will affect waste package performance.	

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 4 of 14)

WBS	Test objectives	Work requirements	Data needs
		W.2.14.B Determine to what extent weathered or altered basalt affect radionuclide release and retardation. W.2.15.B Determine if the geochemical and hydrologic properties of the engineered barrier system will permit the NRC performance objectives to be met. W.2.17.B Determine how Eh, pH, and PO_2 change with time in the vicinity of the container and packing material. W.2.18.B Determine the effects of gamma and alpha radiation on groundwater, basalt plus groundwater, and radionuclide release and retardation mechanisms. W.2.19.B Develop techniques for in situ measurement of Eh and pH.	

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 5 of 14)

WBS	Test objectives	Work requirements	Data needs
L233	Provide sufficient data on radionuclide solubility, sorption, and colloid formation to allow reliable prediction of radionuclide release and transport in the waste package and the repository horizon.	W.2.6.B Determine what natural analogs of waste package components can be used to verify and predict the compatibility of the waste package with the repository environment. W.2.7.B Determine what part solubility, sorption, and colloid and particulate formation play in the transport of radionuclides through the packing material and repository backfill with and without alpha and gamma radiation. W.2.11.B Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill. W.2.18.B Determine the effects of gamma and alpha radiation on groundwater, basalt plus groundwater, and radionuclide release and retardation mechanisms.	1. Solubility estimates from oversaturation 2. Solubility estimates from undersaturation 3. Characterization of precipitated solids 4. Speciation of radionuclides in solution 5. Radionuclide sorption - desorption coefficients and isotherms 6. Elution curves for radionuclides from engineered barriers 7. Groundwater composition 8. Solids composition 9. Radionuclide distribution among colloids - groundwater and solids 10. Elution curves for radionuclides from colloidal particles 11. Radiation effects (radiolysis of groundwater containing methane and basalt)

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 6 of 14)

WBS	Test objectives	Work requirements	Data needs
L234	Provide sufficient data on the reference and backup containment materials exposed to the simulated environment of a nuclear waste repository in basalt to assess their ability to meet design reliability requirements and NRC performance objectives.	W.2.3.B Determine effects of packing material, radiation, repository water composition, and temperature on the corrosion and mechanical behavior of container materials. W.2.16.B Determine effects of packing materials on the corrosion mechanisms for the container in presence and absence of radiation.	For each candidate container material determine: 1. Strength 2. Ductility 3. Stress intensity factors 4. Crack propagation behavior 5. Corrosion behavior - Uniform corrosion - Pitting - Crevice - Intergranular - Bacterial 6. Effects on corrosion of: - Radiation - Hydrogen - Nitrogen - Methane - Packing materials - Water chemistry 7. Container temperature limit

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 7 of 14)

WBS	Test objectives	Work requirements	Data needs
L235	Provide sufficient data on the candidate packing materials exposed to the simulated environment of a nuclear waste repository in basalt to assess their ability to meet design and reliability requirements and NRC performance objectives.	W.2.4.A Determine the maximum operating temperature limits for waste forms, packing materials, container, and host rock. W.2.4.B Determine the rate that Eh, pH, and temperature conditions in the packing material/repository water return to "ambient" conditions after repository sealing. W.2.8.B Determine when and how water contacts the repository backfill, waste package packing material, container, and waste form. W.2.9.B Determine the effect of radiation on the physical, mechanical, and chemical properties of waste package packing material. W.2.10.B Determine the effectiveness of the packing material in restricting the flow of water to and around the container.	For the candidate packing materials determine: 1. Hydraulic conductivity 2. Diffusion coefficients for groundwater 3. Resaturation temperature and time 4. Vapor hydraulic conductivity 5. Swelling pressure 6. Thermal conductivity 7. Radionuclide retardation factors 8. Radionuclide effective diffusion coefficients 9. Radionuclide distribution coefficient 10. Hydrothermal alteration products: - Chemical composition - Crystal structure - Radionuclide context - Particle size - Volume percent

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 8 of 14)

WBS	Test objectives	Work requirements	Data needs
			11. Groundwater alteration 12. Shear strength 13. Radiation effects 14. Material temperature limit
L241	Conduct engineering studies and develop requirements for the design of reliable waste packages for a nuclear waste repository in basalt that will meet the NRC performance objectives.	W.3.1.C Determine what factors of safety and waste package component reliability are necessary to achieve the NRC performance objectives. W.3.2.C Design waste packages so that accidental release of radionuclides to unrestricted areas are within the limits specified in 10 CFR 20. W.3.3.C Design the waste packages so that they may be retrieved at any time during the operating period if necessary. W.3.5.C Determine the mechanical loads on a waste package container as a function of time during handling, transporting, and emplacing and during unforeseen events after emplacement.	(To be added on next update of BMTP due 9/30/84)

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 9 of 14)

WBS	Test objectives	Work requirements	Data needs
		W.3.6.C Determine the design and reliability requirements for waste packages and components for emplacement in a nuclear waste repository in basalt. W.3.10.C Determine conditions that might affect criticality and evaluate criticality potential within and between waste packages. W.3.11.C Complete engineering analysis of failure modes for life history of the waste package and estimate these contributions towards failure. W.3.12.C Complete waste package advanced conceptual design requirements and designs for commercial, defense, and spent fuel waste forms. W.3.13.C Prepare waste package preliminary and final design requirements to complete designs for commercial, defense, and spent fuel waste forms.	

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 10 of 14)

WBS	Test objectives	Work requirements	Data needs
L242	Conduct design development testing leading to the selection of final designs for reliable waste packages for commercial and defense high-level wastes and spent fuel for a nuclear waste repository in basalt that will meet the NCR performance objectives.	W.3.4.C Develop field, engineering, and in situ test plans needed to meet design and performance modeling and conduct tests. W.3.7.C Determine development needs and conduct welding and non-destructive examination methods for the waste container. W.3.8.C Demonstrate remote welding and non-destructive examination of the closure welds on a waste package container. W.3.9.C Conduct tests and engineering studies necessary to provide data for the preparation of waste package design requirements.	(To be added on next update of BMTP due 9/30/84)
L251	Develop models to define radionuclide release from the waste form and behavior in the waste package and geochemical environment of a nuclear waste repository in basalt.	W.2.5.A Determine the waste package containment time and radionuclide release rate necessary to assure releases from the underground facility are within the NRC numerical performance objectives.	(To be added on next update of BMTP due 9/30/84)

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 11 of 14)

WBS	Test objectives	Work requirements	Data needs
		W.2.8.B Determine when and how water contacts the repository backfill, waste package packing material, container, and waste form.	
		W.2.11.B Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill.	
		W.2.12.B Determine what waste package containment time and radionuclide release rates are necessary to assure the releases from the underground facility are within the NRC numerical performance objectives.	
		W.2.16.B Determine effects of packing materials on the corrosion mechanisms for the container in presence and absence of radiation.	

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 12 of 14)

WBS	Test objectives	Work requirements	Data needs
		W.4.1.D Determine when, how, and at what rate radionuclides are released from the waste form, packing material, and repository backfill. W.4.7.D Develop and validate radionuclide transport model for the waste package. W.4.9.D Predict changes in chemical environment surrounding the waste package with time.	
L252	Develop models to predict waste package performance and provide reliability requirements for waste packages sufficient to meet the NRC performance objectives.	W.3.10.C Determine conditions that might affect criticality and evaluate criticality potential within and between waste packages. W.2.4.A Determine the maximum operating temperature limits for waste forms, packing materials, container, and host rock. W.3.6.C Determine the design and reliability requirements for waste packages and components for emplacement in a nuclear waste repository in basalt.	(To be added on next update of BMTP due 9/30/84)

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 13 of 14)

WBS	Test objectives	Work requirements	Data needs
		W.4.2.D Determine when and how the water contacts the repository backfill, waste package packing material, container, and waste form. W.4.3.D Develop a quantitative waste package reliability plan and procedures to demonstrate the reliability of designs and determine importance of specific uncertainties in system performance. W.4.6.D Develop and validate a waste package degradation model to describe failure modes of container and packing material. W.4.8.D Determine effect of temperature and stress on the host basalt.	

TABLE 4-2. Relationship Among Waste Package and Near-Field Geochemistry Test Objectives, Work Requirements, and Data Needs.* (Sheet 14 of 14)

WBS	Test objectives	Work requirements	Data needs
L253	Provide sufficient data from field/engineering testing and in situ monitoring to confirm waste package design and performance predictions	W.4.4.D Identify and develop test plans needed for measuring the behavior of full sized waste packages under conditions that simulate as closely as possible those existing in a nuclear waste repository in basalt. Conduct the tests to meet program schedules. W.4.5.D Develop in situ test plans for monitoring waste packages in a suitable below-grade test facility.	(To be added on next update of BMTP due 9/30/84)

*These data needs are repeated in each subactivity of Section 5.0 where the range of test parameters and test and analytical equipment/techniques are also included.

Note: BMTP = Barrier Materials Test Plan
NRC = U.S. Nuclear Regulatory Commission
WBS = Work breakdown structure

5.0 TEST SUBJECTS

5.1 INTRODUCTION

The justification for developing the data needed to support waste package design and performance assessment modeling was discussed in Section 4.0 together with a table of data needs for the barrier materials test program. Descriptions of data needs are repeated and testing parameters and techniques to be used to develop the required data are described in this section. The testing techniques are based on procedures that are approved or in the review and approval process. A listing of the current test procedures is shown in Section 6.0.

Section 5.1 is presently composed of two activities: (1) Waste Forms and (2) Barrier Materials. The Design and Development and Performance Evaluation activities will be added during the next update of the BMTP by September 30, 1984. In each of these activities there are subactivities in which data needs are again identified in tabular form, together with associated testing techniques and the specific use for the test data to be generated. The summary of testing to date and planned testing are discussed.

Prior to the initiation of tests or series of tests identified in the tables of data and the testing needs included in each subsection to follow, a test specification will be prepared. The specification will include such items as test matrices that define the number of test variations and replications, identification of all variables, variations in the values of the variables, test procedures to be used, and any additional information that will permit the NRC to predict the usefulness of the test results to the repository licensing activities.

Section 5.1 also contains logic networks for each subactivity to define work flow and the data inputs to the waste package design effort, performance assessment, and repository design and licensing activities.

5.1.1 <u>Waste Forms</u>

5.1.1.1 <u>Acquisition of Waste Forms and Waste Form Data</u>.

5.1.1.1.1 <u>Introduction</u>. The BWIP is testing and designing a nuclear waste repository in basalt capable of accepting several types of DOE-selected reference waste forms. To date, both commercial and defense waste form systems have been identified for consideration by the BWIP. The range of radionuclide inventory to be considered by the BWIP for reference cases of commercial wastes spans the full range from light water reactor (LWR) spent fuel to high-level waste produced by spent fuel reprocessing of commercial high-level waste (CHLW) to transuranic (TRU) wastes, both remote handled (RHTRU) and contact handled (CHTRU) types. Defense wastes presently being considered by the BWIP consist of defense high-level waste (DHLW) resulting from reprocessing of defense reactor fuel. Currently, the

DOE-identified reference case waste forms for commercial wastes consist of spent LWR fuel, including both pressurized water reactor (PWR) and boiling water reactor (BWR) fuels, and several candidate borosilicate glasses for use with high-level wastes from reprocessing. Reference waste forms have not been defined yet for the commercial TRU-type wastes. The present reference waste form type for DHLW is borosilicate glass. Both commercial and defense waste form systems have undergone selected development of alternate waste form types, with crystalline ceramics identified as likely candidates for such future waste form applications. The BWIP is establishing programs on testing, data acquisition, and analysis (within the context of DOE guidance on reference waste form systems and their quantities and NRC and EPA regulatory criteria on nuclear waste disposal systems) in order to assess the role of wastes and waste forms in determining the performance of the repository system.

The objective and justification for this set of tasks* on waste form materials, data, and acceptance requirements and specifications are presented in the following subsection. Later subsections present a summary description of specific activities currently planned for each major set of subtasks. The engineered barrier materials testing, analysis, and design programs supported by these subtasks are also identified.

5.1.1.1.2 Objective and Justification. The primary objective of the waste form materials tasks is to directly support the needs of the BWIP Engineered Barriers Department waste/barrier/rock interactions testing program with respect to definition, selection, preparation, and initial characterization of waste form materials. Section 5.1.2.2.2 provides a discussion of the objectives and justification for the waste/barrier/rock interactions testing program. The objective of the waste form reference data acquisition tasks is to acquire data available to support the needs of testing, design, and analysis activities. Specific examples include the experimental data and predictive information on waste and waste form compositions (radioactive and nonradioactive constituents), decay heat load, and various physical, chemical, and radiological properties and characteristics. The remaining major subtask is the development of the requirements, and eventually the specifications, to be applied in judging which waste forms are acceptable for the receipt, packaging, and emplacement in the repository. The justification for this development activity is the obvious need for such requirements and specifications to assist in ensuring compliance with the conditions of the operating license for the repository.

5.1.1.1.3 Summary of Scheduled Tasks. Table 5-1 summarizes the task categories of the project on acquisition of waste form materials and reference data on wastes and waste forms, the nature of each task, the specific subtasks identified to date, and the application or support provided to the overall project by each task and subtask. The waste form

*Tasks and subtasks are used in this subsection to denote elements of work that are at a lower tier than subactivities (see Fig. 1-1).

TABLE 5-1. Summary of Scheduled Tasks. (Sheet 1 of 2)

Task category	Task activity	Specific subtask	Application to design and performance issues
1. Waste form material	Prepare and characterize for testing		
	• LWR spent fuels	Simulated LWR spent fuel (nonradioactive dopants) for subcontractor (Arizona State University) testing	Direct support of W.1.2-1 and waste/barrier rock/interaction testing program
		PWR and BWR spent fuels of normal and off-normal history (design, fabrication, and irradiation)	
		Turkey Point reactor PWR (normal) available 9/30/83	
		H. B. Robinson II reactor PWR (ATM-101) (normal) available 1/31/84	
	• CHLW (waste forms)	A supercalcine loaded with nonradioactive dopants in simulation of a CHLW for subcontractor (Arizona State University) testing.	Direct support of W.1.2, W.2.4, W.2.5, and waste/barrier/rock interaction testing program
		PNL 76-68 borosilicate glass loaded with a nonradioactive simulation of a CHLW for subcontractor (Arizona State University) testing	
		Tracer-doped PNL 77-260 borosilicate glass - early reference glass for Barnwell CHLW, (Slate et al., 1981)(^{238}U, ^{239}Pu, ^{237}Np, ^{241}Am, and ^{99}Tc), available 9/30/84	
		Tracer-doped PNL 76-68 borosilicate glass (^{238}U and ^{99}Tc), available 12/30/82	
		Tracer-doped PNL 76-68 borosilicate glass (^{238}U, ^{239}Pu, and ^{237}Np), available 12/31/82	
		High-level doped BWIP Glass A (ATM-6) (PNL Interim Barnwell Process glass, i.e., replacement of PNL 77-260) (^{238}U, ^{239}Pu, ^{240}Pu, ^{237}Np, ^{244}Cm, ^{99}Tc, ^{137}Cs, and ^{75}Se), available 9/30/83	
		High-level doped BWIP Glass B (^{238}U, ^{241}Am, ^{226}Ra, ^{232}Th, ^{113}Sn, and ^{75}Se), available 3/31/84	
		Actual spent fuel waste fully loaded into PNL 76-68 borosilicate glass (ATM-5) available 4/31/83	

TABLE 5-1. Summary of Scheduled Tasks. (Sheet 2 of 2)

Task category	Task activity	Specific subtask	Application to design and performance issues
		High-level doped West Valley Vitrification Project reference borosilicate glass (dopants to be determined) available 12/31/85	
	• DHLW (waste forms)	Simulated Savannah River DWPF waste form. Frit 131 with nonradioactive dopants, provided by SRL, available 6/83.	Direct support of W.1.2, W.2.4, W.2.5, and waste/barrier/rock interaction testing program
		High-level doped BWIP Glass D, Savannah River DWPF reference waste form, Frit 165 borosilicate glass (^{238}U, ^{239}Pu, ^{241}Am, ^{237}Np, ^{99}Tc, and ^{152}Eu), available 3/31/84	
		Hanford high-level doped waste form based on B Plant Immobilization Pilot Plant Project (to be determined)	
	• TRU waste forms	Commercial TRU (to be determined)	
		Defense TRU (to be determined)	
2. Waste form reference data	Obtain referenceable characterization data, predicted values, and information on DOE-identified reference waste form systems	Types, sources, quantities, composition (radioactive and nonradioactive), radiation and thermal (decay heat) inventory	Supports all major design, testing, and analysis of the BWIP (issues: W.1.1, W.1.2, W.1.2-1, W.11, W.15, W.18, 4.2.17, 4.2.14, 4.2.24, W.2.31, W.2.32)
3. Waste form acceptance requirements	Develop requirements	SD-BWI-CR-018 (draft being revised as per DOE and subcontractor reviews)	Supports W.1.1 and development of advanced conceptual design requirements and design tasks
	Develop preliminary specifications	FY 1986	Supports W.1.1
	Develop final (draft) specifications	FY 1989	Supports W.1 and the compliance with terms of repository license

Note: BWIP = Basalt Waste Isolation Project
BWR = Boiling water reactor
CHLW = Commercial high-level waste
DHLW = Defense high-level waste
DOE = U.S. Department of Energy
DWPF = Defense Waste Processing Facility
LWR = Light water reactor
PNL = Pacific Northwest Laboratory
PWR = Pressurized water reactor
SRL = Savannah River Laboratory
TRU = Transuranic

materials preparation and characterization tasks are divided into the categories of LWR spent fuel (both PWR and BWR types), CHLW forms, DHLW forms, and TRU waste forms (both commercial and defense).* Lastly, the task categories for development of the BWIP requirements, preliminary specifications, and final (draft) specifications for waste form acceptance are presented.

5.1.1.1.4 <u>Summary of Task Plans and Status to Date</u>.

5.1.1.1.4.1 <u>General Discussion</u>. The choice sequence of waste form materials being prepared and characterized in support of BWIP testing programs (e.g., waste/barrier/rock interactions testing) usually begins with relatively simple systems and then proceeds on to more complex representatives of each system. This is a typical scientific approach for addressing technical issues involving highly complex materials and/or conditions (environment). This approach is balanced against the practical need to minimize the number of specimen material subtypes that must be tested in order to characterize a given waste form type as a variable in the near-field geochemical system. The major waste form systems identified by the DOE for use in the NWTS Program design and testing programs were noted in Section 5.1.1.1.1.

The process of defining the composition of the waste forms to be tested usually focuses on the waste constituents. For actual spent fuel, the process is primarily reduced to that of selection and acquisition. The PNL/Materials Characterization Center is currently preparing, with the assistance of the NWTS Program, a document that defines the criteria proposed for selecting, preparing, and characterizing the LWR spent fuel materials to be tested. For actual high-level waste form reprocessing, the matter is primarily reduced to decisions regarding waste loading level, compositional adjustments to improve the simulation of the given reference waste system, or to facilitate analysis of test products (e.g., key radionuclides in solution samples). Establishing the desired compositional complexity of simulated waste forms involves specifying both the elemental and isotopic composition. The overall process is keyed against the known or predicted composition (elemental and isotopic) of each waste form system currently identified by the DOE as a reference system for the NWTS Program. Next, a review is made of the lists(s) of priority or key elements (isotopes) defined by performance assessment considerations (e.g., abundance, half life, toxicity, solubility, etc.) and screening techniques. A prioritized list is prepared of proposed dopants (radioactive and/or nonradioactive) to be used in simulating the reference waste stream composition. The proposed list of dopants is then reviewed with respect to

*See Table 5-4 in Section 5.1.2.2 for a breakdown of the types of testing supported by the tasks on waste form materials and reference data acquisition. The waste form reference data task is briefly described with respect to identified DOE reference waste form systems.

limitations of the analysis of test products (in particular, solution samples from the hydrothermal interactions testing) and limitations imposed by fabrication facilities and dopant availability and cost. Potential interferences in or between analyses of given elements/isotopes (radioactive or nonradioactive) are identified. If a given interference is considered signficant, an effort is made to minimize the problem by means of changes in proposed analysis technique(s), procedure(s), and/or dopant selection (element and isotope(s)). For waste form systems simulated using only nonradioactive dopants, or radioactive dopants that are present at very low activity levels and not going to be analyzed by radiochemical techniques, the process of defining the final dopant composition is of only moderate complexity. Compositions to be made with only one or two radioactive dopants, for purposes of radiometric detection and measurement, are also moderately easy to accommodate. In cases of waste form simulations where the objective is to incorporate as many radioactive dopants as practicable, the process is complex and usually requires several iterations to achieve a composition that will not (of itself) impair, by interferences, analysis complexity, or cost, the pursuit of the objectives of the testing program.

5.1.1.1.4.2 Acquisition of Specific Waste Form Materials. Acquisition of waste forms from the Materials Characterization Center that have been prepared (monoliths, crushed, and size particles, etc.) for BWIP testing programs is the responsibility of this task. Documentation of these preparations and the baseline characterization necessary to certify them as approved test materials is the responsibility of the Materials Characterization Center. This program has been developed to support the development of waste forms for testing in accordance with requests made by the NWTS Program repository projects.

Table 5-1 provides a summary of all waste form materials prepared for or planned by the BWIP to date. The following three simulated CHLW form materials were made for the BWIP and used in the "cold" (nonradioactive) waste form testing by subcontractor programs: (1) a borosilicate glass (PNL 76-68) doped with cold constituents, (2) a super-calcine ceramic doped with cold constituents, and (3) a ceramic composition doped with cold constituents in a general chemical simulation of LWR spent fuel. The first two materials were used in the Arizona State University testing program and the latter material was tested at Temple University. At present, three "tracer-" (low-level) doped (i.e., low concentrations of radioactive isotopes) borosilicate glasses were acquired for initiating interactions testing of CHLW forms using facilities approved only for cold- or tracer-doped specimen materials. Radioactive tracer dopants in the three materials consisted of (1) ^{99}Tc, (2) ^{237}Np and ^{239}Pu, and (3) ^{237}Np, ^{241}Am, ^{239}Pu, and ^{99}Tc, respectively, with the waste form (glass) being PNL 76-68 in the first two and PNL 77-260 in the third. Uranium is present as a cold dopant in all three of these materials. The first high-level, selectively doped CHLW form materials being prepared are scheduled for use in the BWIP hot cell supported (i.e., for test cell loading and unloading) testing facilities presently consisting of static system testing at the 325 Building, 300 Area, and flowthrough system testing at 222S Building, 200 West Area, at the Hanford Site. At present, these high-level, selectively doped materials consist of a companion set of glasses (Interim

Barnwell Process Glass, an improved replacement for PNL 77-260) tailored to include as many radioactive dopants as practicable. The composition and recipe of radioactive and cold dopants were carefully tailored to minimize interferences during analysis of testing solution samples. Although not keyed against the composition of specific waste age, the radioactive dopant concentrations used do, in effect, correspond radiologically to a waste that is a few hundred years old. The primary member of the set is the BWIP Glass A, or ATM-6 (as the Materials Characterization Center has designated it) which contains ^{238}Pu, ^{226}Ra, ^{232}Th, ^{244}Cm, ^{99}Tc, ^{137}Cs, and ^{75}Se as the radioactive dopants added for use in providing a radiation environment and for the analytical sensitivity offered by radiometric analysis techniques. The secondary member of the set is Glass B, which contains ^{241}Am, ^{226}Ra, ^{232}Th, ^{113}Sn and ^{75}Se as radioactive dopants. Glasses A and B both contain uranium as a cold (depleted uranium) constituent. Lastly, a PNL 76-68 glass that contains actual LWR spent fuel PWR wastes, available from an earlier laboratory-scale waste vitrification program, has been prepared and currently designated for interactions testing starting in FY 1985. A high-level doped waste form (borosilicate glass) representative of the West Valley, New York, Vitrification Facility has been planned but not fully defined as yet.

The DHLW form materials available, or specified at present, are representative of the Savannah River Defense Waste Processing Facility. The first is a cold dopant material using the current reference design glass (Frit 131) and was provided to the BWIP by Savannah River Laboratory. The second material, as currently planned, will involve Frit 165, the current primary Savannah River Laboratory glass for waste form performance testing, and will contain ^{238}Pu, ^{241}Am, ^{237}Np, ^{99}Tc, ^{137}Cs, and ^{144}Ce as radioactive dopants. The fission product and actinide dopant recipe will be keyed against the predicted composition of a 300-yr-old waste mixture of Stage 1 (sludge) and Stage 2 (supernate). The 300-yr waste age was selected in relation to the NRC regulatory criteria regarding the container having to provide containment for at least 300 yr after waste package emplacement in the repository. Savannah River Laboratory will provide the frit as mixed with the inert constituents from the waste processing stream, and the waste form fabrication, etc., will be done for the BWIP by the Materials Characterization Center. Consideration of DHLW originating from other defense-waste-producing sites must await additional guidance from the DOE regarding approval for consideration and definition of the reference waste form systems.

Waste form materials will be prepared as needed to determine the effects upon waste/barrier/rock interactions testing results of such conditions as (1) simulation of aged waste form materials, (2) the redox condition of constituents in waste form materials, and (3) other variables identified as the waste/barrier/rock interactions testing program matures. Item 1 refers to simulation of the aged condition of waste-loaded borosilicate glass waste forms (e.g., devitrification products, etc.). Investigation of the effects of aging on the gross chemical inventory of waste-loaded borosilicate glass waste forms has been initiated as part of the testing program. The valence state of waste form constituents, especially those in the waste, is an important consideration relative to their solubility and interactions behavior in the hydrothermal test solution. The effort to define the appropriate scope of the overall materials development, characterization, testing, and analysis program needed to address this technical issue is currently in the early stages of definition. Among other things, more information is needed about potential redox controls being considered in the waste form (e.g., glasses, crystalline ceramics, etc.).

5.1.1.1.4.3 Waste Form Characteristics. Data, predictive values, and information characterizing waste forms are actively acquired from DOE and subcontractors to support the BWIP testing, design, and analysis programs. The BWIP participates, with the other NWTS Program projects, in guiding development of future baseline documents on reference waste form systems, such as the Mined Geologic Disposal System Requirements document. Information is also acquired for possible inclusion in internal BWIP documentation, e.g., the data package on reference waste form characteristics and in support of the internal information needs of the project.

5.1.1.1.4.4 Waste Form Acceptance Requirements and Specifications. The DOE/NWTS-33 document series, (1) through (4) (NWTS, 1981, 1982a, 1982b, 1982c), serves as the general NWTS program guidance in the site-specific investigations of mined geologic storage as a licensable system for the disposal of nuclear wastes. The DOE/NWTS-33(1) (NWTS, 1982a) discusses the general program objectives, functional requirements, and system performance criteria; DOE/NWTS-33(2) (NWTS, 1981) and (3) (NWTS, 1982b) present the general site and repository performance criteria, respectively; and DOE/NWTS-33(4a) (NWTS, 1982c) discusses the general functional requirements and performance criteria for waste packages containing high-level waste either in processed waste forms or as spent fuel. Work is still underway within the NWTS Program to document the general functional requirements and performance criteria for waste packages containing TRU wastes and on documenting the specific character of TRU wastes, including both CHTRU and RHTRU wastes.

In FY 1983, the BWIP produced a document (Rockwell, 1983a) for DOE and subcontractor review that proposed the waste form acceptance requirements for the BWIP covering CHLW and DHLW from spent fuel reprocessing and commercial spent fuel itself. The DOE and selected subcontractors have reviewed the document, and the BWIP is currently working to disposition the review comments and will revise and issue the document later in FY 1984. The requirements document is the first stage of the BWIP effort to develop site-specific waste form acceptance specifications. The next step will be the development of preliminary acceptance specifications that will be followed by final acceptance specifications. The Materials Characterization Center at PNL is presently working in support of the BWIP acceptance specifications task by developing a compliance test relative to the requirements and specifications on allowable radionuclide release from reference waste forms at the request of the BWIP. Development tasks associated with other compliance tests have not been defined as yet, although the Materials Characterization Center does intend to complete an initial compliance test during FY 1984.

5.1.1.1.5 Logic Diagram. The flow of work required to provide characterized waste forms for hydrothermal testing is shown in Figure 5-1.

5.1.2 Barrier Materials

5.1.2.1 Waste/Barrier/Rock Interaction.

5.1.2.1.1 Introduction. The laboratory testing activities described in this subsection cover three areas: (1) basalt/water hydrothermal experiments scoped to provide baseline data on the waste package environment in a nuclear waste repository in basalt; (2) since it is of great importance to the success of the materials testing program, research to develop Eh and pH sensors that can be incorporated into the autoclaves used for hydrothermal testing to enable direct measurements of these two key parameters during test runs; and (3) waste/barrier/rock interaction studies needed to determine radionuclide operational solubility limits (or steady-state concentrations) and stability of waste package component materials under site-specific conditions.

The baseline data expected from basalt/water hydrothermal experiments will include data on steady-state solution chemistry, Eh, pH, and alteration products formed as a function of temperature, water to basalt mass ratios, and basalt particle size. The results of basalt/groundwater hydrothermal experiments will provide data that are essential for (1) testing and selection of container and packing materials, (2) establishing radionuclide sorption and solubility effects, and (3) interpreting data obtained from experiments using basalt plus waste forms and barrier materials.

Waste/barrier/rock interaction studies emphasize the determination of operational solubility limits (or steady-state concentrations) for radionuclides present in proposed waste forms, both alone and in the presence of other barrier materials (waste package components), under site-specific hydrothermal conditions (Apted, 1982). The resulting data on solution composition and solid mineral alteration products are used in conjunction with hydrologic flow data for determining radionuclide release rates from the engineered barriers system and disturbed rock zone (Wood, 1980; Wood and Rai, 1981; Chambre et al., 1982). These data are, in turn, used to (1) establish the need for specific barriers (components) for the waste package design, (2) confirm the overall performance of the waste package design, and (3) identify specific radionuclides that may require special design modifications of the packing materials component. Waste package radionuclide release rates, calculated from solution data obtained in waste/barrier/rock interaction tests, are also key input parameters to the overall safety assessment of the repository. The current testing effort, plans for additional basalt/water testing and development of pH/Eh sensing techniques, and waste/barrier/rock interaction studies are discussed in the remainder of Section 5.1.2.1.

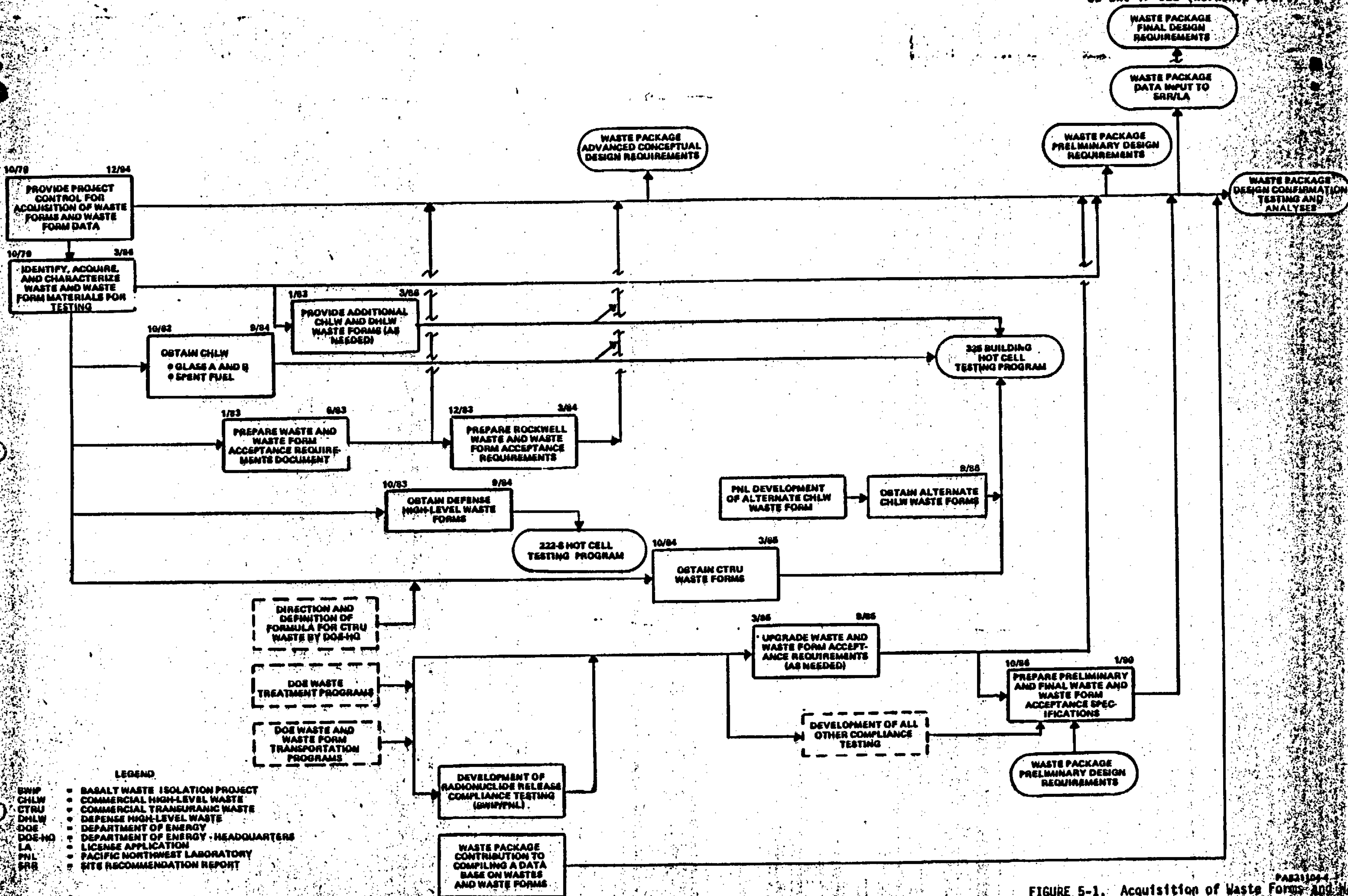


FIGURE 5-1. Acquisition of Waste Forms and Waste Form Data Logic Diagram.

5.1.2.1.2 Objectives and Justification.

5.1.2.1.2.1 Basalt/Water Interactions. The objective of basalt/water hydrothermal interaction testing is to provide sufficient data on the waste package environment of a nuclear waste repository in basalt in response to the addition of waste form radiogenic heat and radiation to establish limits on test parameters for planned barrier materials testing. The data to be collected include changes in groundwater composition (solution chemistry), Eh, and pH, as well as characterization of alteration phases.

The addition of heat and radiation caused by the emplacement of waste containers will result in groundwater/rock interactions that will cause changes in the solution chemistry, Eh, and pH. Such hydrothermal basalt/water interactions also will cause the formation of secondary mineral alteration products such as clays and zeolites. Changes in solution chemistry are of great importance to repository performance, since the solubility and sorption of most radionuclides are dependent on solution Eh and pH as well as the concentrations of complexing agents such as fluoride, chloride, and carbonate. Also, changes in solution chemistry, Eh, and pH can have a profound effect on the corrosion behavior of container materials and the stability of packing materials. The formation of alteration products also is of great importance to repository performance because some of these alteration products can incorporate radionuclides within their crystal structure, thus rendering them immobile. Alteration products such as zeolites and clays also have excellent sorptive properties and can thus retard the passage of radionuclides into the accessible environment. Information on changes in the Eh, pH, solution chemistry, and alteration products in response to changes in temperature is essential for assessing the performance of waste packages and the nuclear waste repository in basalt. The information obtained from these tests will also provide a basis for interpreting the results of the more complex waste/barrier/rock interaction tests.

5.1.2.1.2.2 Waste/Barrier/Rock Interactions. The objective of the BWIP waste/barrier/rock interactions testing is to provide sufficient data on the interactions among waste package components and the host rock exposed to an environment simulating that of a nuclear waste repository in basalt in order to assess radionuclide release rates from the waste package and its ability to meet the NRC performance objectives.

The waste package performance assessment data requirements are based on the performance objectives identified by the NRC (NRC, 1983a). Among the objectives are two that require that the waste package provide substantially complete containment of high-level waste for not less than 300 yr or more than 1,000 yr, and that the release rate of any radionuclide from the engineered barrier system (waste package and underground facility) following the containment period shall not exceed one part in 10^5/yr of the inventory present at the close of the containment period.

It has been demonstrated (Wood, 1980; Chambre et al., 1982) that release rates of long-lived radionuclides can be calculated from solubility or steady-state concentration limits (see Appendix B). The final radionuclide release rates obtained from waste/barrier/rock interaction system tests serve as direct source terms for the performance assessment of the repository system. By closely simulating and controlling relevant environmental parameters, including groundwater flow rate, these tests provide release limits with quantified uncertainties that are required for performance assessment.

These same tests also have a secondary objective that is related to the waste package design activity. Results from hydrothermal tests on reference waste forms are required to determine the need for multiple barriers in the conceptual waste package design in order to assure acceptably low waste package release rates. A progressive series of hydrothermal tests on the waste form, waste form/basalt, waste form/container, and waste form/container/basalt, etc. will be used to detect deleterious effects, if any, of one barrier on the function of another, i.e., the compatibility of barriers can be established. For example, the presence of container corrosion products may lead to the formation of radionuclide-bearing colloids and, consequently, release rates higher than those imposed by measured solubility limits. Once alerted to an unacceptable synergistic interaction from hydrothermal testing, further waste package design modifications (such as the inclusion of packing materials) may be necessary to alleviate or mitigate this potentially undesirable effect. Finally, the results of hydrothermal tests on the waste/barrier/rock interaction system can be used to identify key radionuclides that are released at greater than acceptable rates and may require special design modifications to existing barriers, such as special tailoring agents for the packing materials. The radionuclides ^{14}C and ^{129}I, for example, are expected to show high solubility limits and low sorption tendencies. Test data may reveal that it is necessary to add special reactive chemical agents to the packing material to assure satisfactory isolation of these radionuclides within the waste package.

One approach to performance assessment has been to utilize existing literature on radionuclide solubilities to calculate release rates (Early et al., 1982; Chambre et al., 1982); however, there are limitations to this approach. The fact that such solubility data were not obtained under site-specific conditions is of the most concern since temperature, pressure, pH, Eh, and groundwater composition can all affect radionuclide solubility values. Such calculations do, however, help to identify the radionuclides and performance parameters of the waste package that are key for meeting proposed federal regulations. With the time constraints imposed by the Nuclear Waste Policy Act of 1982 and the questionable appropriateness of equilibrium solubility values in a demonstrably nonequilibrium system, the BWIP cannot embark on an extended research program to determine solubilities of a variety of radionuclide-bearing solids over a range of environmental conditions and still provide defensible data within the time available to complete the testing program. For this reason, the BWIP has adopted a direct approach for obtaining operational solubility and/or steady-state concentration data on reference nuclear waste forms by hydrothermal testing under controlled conditions that simulate expected conditions in a nuclear waste repository in basalt. This testing approach can be summarized by the following three activities:

- Measuring solubility/steady-state radionuclide concentration
- Identifying, where possible, radionuclide-bearing colloids and hydrothermal alteration products that contribute to solubility-limiting radionuclide release
- Determining effects of variation in physicochemical parameters on observed solubility/steady-state radionuclide concentrations
- Evaluating the interactive effects of barrier materials on the release rate of radionuclides from the very near-field environment.

This approach measures the performance of the waste package system as a whole, assuming that the hydrothermal reactions and interactions controlling radionuclide release rates are more complex than a simple summation of individual equilibrium solubility reactions.

5.1.2.1.3 Summary of Data Needs.

5.1.2.1.3.1 Basalt/Groundwater Interaction. Table 5-2 summarizes data to be obtained, what controlled parameters will be used to obtain data, and the application of the data to waste package design and performance modeling. Table 5-3 summarizes the listing techniques, equipment, test parameters, data produced, and analytical techniques to be used.

Basalt/groundwater hydrothermal interaction experiments are designed to provide information on the effect of temperature, water to rock ratio, and basalt particle size on solution composition, Eh, pH, and alteration mineralogy. Some specific experiments are designed to compare the behaviors of different basalt flows or different groundwater compositions under hydrothermal conditions. Other basalt/groundwater experiments are designed to determine the effect of the addition of a component such as methane on the chemical evolution of the system.

An additional series of experiments are planned to determine the oxygen buffering capacity of Grande Ronde Basalt. Oxygen will be introduced into the repository environment during the construction and operation phase. The crushed basalt component of the packing materials has the ability to react with the introduced oxygen in such a way as to return the repository environment to its original reducing condition. However, a given amount of crushed basalt has a finite capacity to reestablish reducing conditions. It is essential, therefore, to experimentally determine the oxygen-buffering

TABLE 5-2. Summary of Data To Be Obtained from Basalt-Groundwater Interaction Testing.

Data category	Data produced	Measured or controlled parameters	Application to waste package design/performance assessment
Repository chemical environment	A. Altered groundwater composition	Temperature, pressure, water to rock mass ratio, particle size, concentration of cations and anions	Groundwater chemistry data are needed to predict interactions between groundwater and radionuclides (i.e., precipitation and complexation). Steady-state groundwater composition data can be coupled with groundwater velocity estimates to calculate the rate of release of radionuclides from the waste package.
	B. Groundwater Eh and pH	Temperature, pressure, water to rock mass ratio, particle size, Eh and pH	The Eh and pH are needed to predict the solubilities and sorption behavior of radionuclides. The data are also necessary in packing material and container corrosion studies to select materials for testing and design of waste packages.
	C. Hydrothermal alteration products	Temperature, pressure, water to rock mass ratio, particle size, composition and mineralogy of hydrothermal alteration products.	Hydrothermal alteration products can immobilize radionuclides by precipitation or sorption. This information will support performance assessment modeling by settling solubility limits based on experimentally observed alteration phases.

TABLE 5-3. Summary of Test Techniques Required for Basalt-Groundwater Interaction Testing.

Test technique	Test equipment	Parameters investigated	Data produced	Analytical techniques
Basalt/water interaction tests	Dickson sampling autoclaves operated at 300 bars pressure	Temperature 100° to 300°C	Steady-state solution composition	Cations: AA, ICP, NAA Anions: ion chromatography Carbonate: total carbon analyzer
		Water to rock mass ratio 1:5 to 1:50		
		Particle size	pH	Room temperature: glass electrode
		-60 to +115 -120 to +230 -16 to +60		At elevated pressure and temperature: zirconia pH sensor
			Eh	Dissolved redox species
				Teflon H_2 diffusion membrane
				Dissolved O_2 measurements
				Electrochemical sensors
			Secondary alteration phases	Optical microscope
				SEM
				Electron microprobe
				X-ray diffraction
				STEM

Note: AA = Atomic adsorption
ICP = Induction coupled plasma
NAA = Neutron activation analysis
SEM = Scanning electron microscope
STEM = Scanning transmission electron microscope

capacity of the basalt. These data will be used in repository design to provide enough crushed basalt in the packing material to ensure that reducing conditions will prevail throughout the lifetime of the sealed repository.

5.1.2.1.3.2 Waste/Barrier/Rock Interaction. Table 5-4 summarizes the categories of waste/barrier/rock interaction testing, the data obtained from these tests, what test parameters are controlled, and the specific application of the data to waste package design and performance assessment. The test categories are divided on the basis of the barriers or combination of barriers that are being tested. Within each category, the data produced relate to the determination of solubility/steady-state limits to radionuclide concentrations. This is considered to be an appropriate, defendable, and conservative approach to waste/barrier/rock interaction testing for obtaining long-term radionuclide release rates from the waste package. Comparisons between the data produced in each test category, in turn, are used for providing design data on need, composition, and compatibility of waste package barriers, as well as for evaluating the performance of the overall waste package system relative to the NRC performance objectives (NRC, 1983a).

Table 5-5 breaks the waste/barrier/rock interactions testing program into three parts based on different experimental approaches. The justification for these approaches is presented in Appendix C. The three test methodologies are:

- Tracer and high-level radioactive waste/barrier/rock interaction tests performed under static (no-flow) conditions
- Radionuclide-doped water/barrier/rock interaction tests performed under static (no-flow) conditions
- Tracer and high-level radioactive waste/barrier/rock interaction tests performed under dynamic (flowthrough) conditions.

The purpose of the first set of tests is to establish the initial release rate of radionuclides from the waste form, identify the alteration solids that control this release, and identify the possible synergistic effects of other waste package components on the performance of the waste form. The second set of tests is required to establish the interactions of radionuclide-bearing groundwater with waste package components and basalt (representing the basalt in the disturbed zones encompassing the waste package) that may retard or reduce the rate of radionuclide release to the far-field. Finally, the third set of tests is needed to establish the correct order of radionuclide interaction with waste package barriers and to demonstrate the effect of groundwater flow rate, and other environmental parameters, on radionuclide release.

TABLE 5-4. Summary of Data To Be Obtained from Waste/Barrier/Rock Interaction Testing. (Sheet 1 of 4)

Data category	Data produced (units)	Measured or controlled parameters	Application to waste package design/performance assessment
1. Waste/water	Solution data • Steady-state radionuclide concentrations (mg/L; µCi/L) • Steady-state cation concentration (mg/L) • Steady-state anion concentration (mg/L) • pH (unitless) • Eh (mV) • Composition of water to use in subsequent testing as groundwater progresses through the engineered barrier system Alteration solids data • Chemical composition (wt%) • Crystal structure (descriptive) • Radionuclide content (p/m wt%) • Grain dimensions (µm) • Proportion (vol% of total solids) Colloidal solids data Same as for alteration solids data	Temperature, pressure, particle size, ratio of solid surface area to volume of groundwater (or ratio of mass of powdered solid to mass of groundwater), flow rate, radiation field, test duration, pH, Eh, initial groundwater composition.	Performance Assessment • Waste/water tests provide the initial release rates of radionuclides from the waste form and establish the need for additional barriers. • Comparison of test data on tracer-loaded and fully radioactive waste forms will aid in the determination of radiation on waste form degradation and radionuclide release rates. • These solution data establish the composition of radionuclide-bearing waters used in tests studying the transport of radionuclides in the waste package and far-field environments (see data categories 5, 6, and 7 of this table). Design Criteria • Release rates of radionuclides calculated from steady-state concentrations obtained in these tests can be compared to draft Federal release rate criteria for the waste package. Performance allocation can be assigned to the waste form(s), and the need for additional barriers (or modification of existing barriers) in the waste package design can be established.

TABLE 5-4. Summary of Data To Be Obtained from Waste/Barrier/Rock Interaction Testing. (Sheet 2 of 4)

Data category	Data produced (units)	Measured or controlled parameters	Application to waste package design/performance assessment
2. Waste/basalt/water	Same as data category 1	Same as data category 1	Performance Assessment • Waste/basalt/water tests provide data on waste form release rates of radionuclides (in the absence of packing material and container) under conditions controlled by the repository host rock. • Establish the fate-of-radionuclides released from the waste form by analysis of alterations solids of basalt that contain or sorb radionuclides. Design Criteria • Determine what redox conditions are imposed by the basalt on groundwater and what effect it has on the release of radionuclides. • Ddmonstrate the formation of suspended colloids, if any, that may form during waste/basalt reaction. Formation of such colloids could lead to excessively high release rates of radionuclides because of transport of radionuclide-bearing colloids.
3. Waste/container/water	Same as data category 1	Same as data category 1	Performance Assessment • Compare steady-state concentration data between waste/water and waste/container/water test. This will confirm if the container, as the barrier located closest to the waste form, may alter waste form release rates.

TABLE 5-4. Summary of Data To Be Obtained from Waste/Barrier/Rock Interaction Testing. (Sheet 3 of 4)

Data category	Data produced (units)	Measured or controlled parameters	Application to waste package design/performance assessment
			• Document alteration (corrosion products that may contain or sorb radionuclides and thus limit long-term release). Design Criteria • Determine if presence of container and/or its corrosion products might have an adverse effect on radionuclide release rates. This could require design modification of container, waste form, or both.
4. Waste/container/packing material/water	Same as data category 1	Same as data category 1	Performance Assessment • Provide overall confirmation of waste package system conformance to Federal release rate criteria. Tests involving flow of groundwater through the several barriers are particularly vital to this conformance testing. • Confirm pre-test estimates as to which radionuclides most closely approach release rates above Federal criteria (i.e., experimentally define "key radionuclides"). • Establish expected waste package release rates to be used as a source term for repository safety assessment. Design Criteria • Confirm overall compatibility between barriers.

TABLE 5-4. Summary of Data To Be Obtained from Waste/Barrier/Rock Interaction Testing. (Sheet 4 of 4)

Data category	Data produced (units)	Measured or controlled parameters	Application to waste package design/performance assessment
			• Identify any radionuclides that are released from waste package above acceptable limits, thus requiring design modification, such as chemical tailoring of the packing material.
5. Radionuclide-bearing water/container	Same as data category 1	Same as data category 1	Performance Assessment • Document alteration products that may limit long-term radionuclide release rates. Design Criteria • Determine if alteration products might form radionuclide-bearing colloids, indicating a potential adverse effect on radionuclide release rates necessitating design modifications. • Assign performance allocation to the barrier for limiting radionuclide transport and/or release.
6. Radionuclide-bearing water/packing material	Same as data category 1	Same as data category 1	Performance Assessment • Same as data category 5. Design Criteria • Same as data category 5.
7. Radionuclide-bearing water/basalt	Same as data category 1	Same as data category 1	Performance Assessment • Same as data category 5. • Establish expected release rate of radionuclides through the repository host rock for repository safety assessment. Design Criteria • Same as data category 5.

TABLE 5-5. Summary of Test Techniques Planned for Waste/Barrier/Rock Testing. (Sheet 1 of 2)

Test technique	Test equipment	Data produced	Range of parameters	Required analytical equipment
1. Static waste/barrier/ rock tests	A. Sampling autoclave (Dickson-type)	Solutions In situ solution data, including steady-state concentration of radionuclides and other stable cations and anions, pH, and Eh Solids Composition and crystal structure of alteration solids, radionuclide content	Temperature: 90° to 300°C Pressure: 0.1 to 30.0 MPa Flow rate: None, agitation Solid/water mass ratio 1:1 to 1:50 Surface area/ volume ratio: 10 to 100 cm^{-1} Particle size: -16 + 60 mesh to -120 + 230 mesh	Solutions Inductively coupled plasma-atomic emission spectrophotometer; total carbon analyzer; ion chromatograph; in situ Eh/pH monitoring probes; thermometers; alpha, beta, and gamma counting devices, pressure gauges Solids Optical microscope; scanning electron microscope; analytical scanning/transmission electron microscope; X-ray powder diffraction
	B. Savannah River Laboratory procedure (basalt cup) - defense waste only	Same as above	Temperature: 60° to 90°C Pressure: 0.1 MPa Flow rate: None Solid/water mass ratio: None specified Surface area/ volume ratio: 0.1 to 10 cm^{-1} Particle size: Monolith	Same as above
	C. Material Characterization center procedure (MCC-14) commercial waste for acceptance test	Same as above (Potential problem of retrograde reaction for tests above 100°C)	Temperature: 60° to 150°C Pressure: 0.1 to 0.5 MPa Flow rate: None, agitated Solid/water mass ratio: 1:1 to 1:10 Surface area/ volume ratio: 10 to 1000 cm^{-1} Particle size: -16 + 60 mesh	Same as above

TABLE 5-5. Summary of Test Techniques Planned for Waste/Barrier/Rock Testing. (Sheet 2 of 2)

Test technique	Test equipment	Data produced	Range of parameters	Required analytical equipment
2. Static doped-water/barrier/rock interaction tests	Teflon vials	Same as above (Steady-state concentration approach as a function of groundwater flow rate)	Temperature: 60° to $90^{\circ}C$ Pressure: 0.1 MPa Flow rate: None Solid/water mass ratio: 1:5 to 1:10 Surface area/volume ratio: 10 to 200 cm^{-1} Particle size: -16 + 60 mesh to -120 + 230 mesh	Same as above
3. Dynamic waste/barrier/rock interaction tests	Flowthrough columns in autoclaves	Same as above (Steady-state concentration approach as a function of groundwater flow rate)	Temperature: 90° to $300^{\circ}C$ Pressue: 5.0 to 30.0 MPa Flow rate: 0.05 to 10^{1} m/yr Solid/water mass ratio: Not applicable Surface area/volume ratio: Not applicable Particle size: -16 + 60 mesh	Same as above

These methodologies are predicated on three basic assumptions regarding the processes controlling radionuclide release rates. The first assumption is that solubility or steady-state limits are the preferable data for calculating long-term release rates. The second assumption is that migration of radionuclides out of the waste package occurs by sequential penetration of barriers by radionuclide-bearing groundwaters. The third assumption is that the data to be produced for design and performance assessment must be oriented toward a "fate-of-the-radionuclide" approach rather than solely on a "fate-of-the-waste form" approach (see Appendix C).

A review of the hydrothermal test equipment needed to produce the data for the waste package design and performance assessment activities is presented in Appendix D. The basic test apparatus for static (no-flow) waste/barrier/rock interaction testing is the Dickson-type sampling autoclave (Fig. 5-2). A flowthrough hydrothermal apparatus of a new design (Fig. 5-3) will provide data on the effect of controlled flow rate on radionuclide release rates from a scaled version of a waste package. The full analytical requirements and instruments for obtaining relevant and defensible hydrothermal test data related to waste package design and performance assessment are also reviewed in Appendix D.

5.1.2.1.4 <u>Summary of Testing to Date</u>.

5.1.2.1.4.1 <u>Basalt/Groundwater Interaction</u>. Hydrothermal tests using Dickson sampling autoclaves (see Fig. 5-2) have been performed for the system Umtanum flow basalt/Grande Ronde Basalt groundwater at temperatures of 300°, 200°, 150°, and 100°C. The basalt to water mass ratio was varied from 1:5 to 1:50 using three crushed basalt particle size ranges: -60 +115, -120 +230, and -16 +60 mesh. The duration of the tests was varied from several tens of hours for the high temperature experiments to greater than 4,000 h for the low temperature experiments. The pressure in all tests was arbitrarily held constant at 30 MPa.

Groundwater that reacted with Umtanum flow basalt in these experiments was shown to be chemically buffered by reacting with coexisting primary and secondary solids in the host rock. Optical examination of reacted basalt fragments did not reveal any alteration of primary feldspars, pyroxenes, or magnetite, but the glassy mesostasis did undergo significant dissolution. Major alteration phases produced as a result of this dissolution included silica, zeolites, potassium feldspar, illite, smectite clay, and amorphous iron oxides. Heulandite, wairakite, chlorite, scapolite, anhydrite, and barite were tentatively identified.

The Eh condition for the basalt/groundwater interaction tests was initially oxidizing (air saturated). During the tests, the Eh value became progressively more reducing as oxygen was consumed by the oxidation of ferrous iron released by the dissolving (glass) mesostasis. Reducing conditions were approached asymptotically with time. A detailed discussion of Eh and pH sensing devices/techniques is contained in Section 5.1.2.1.5.1.

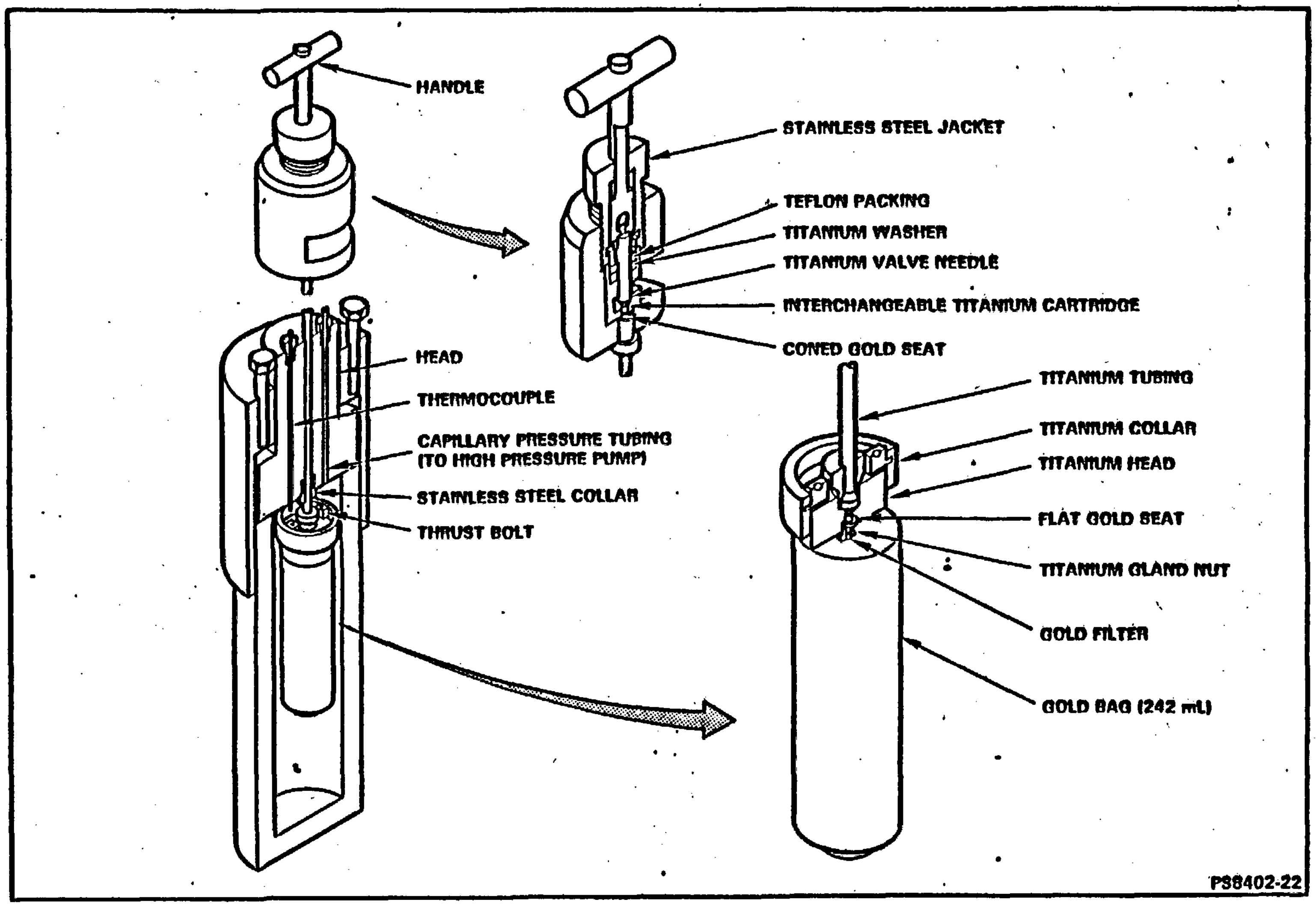


FIGURE 5-2. Dickson-Type Sampling Autoclave.

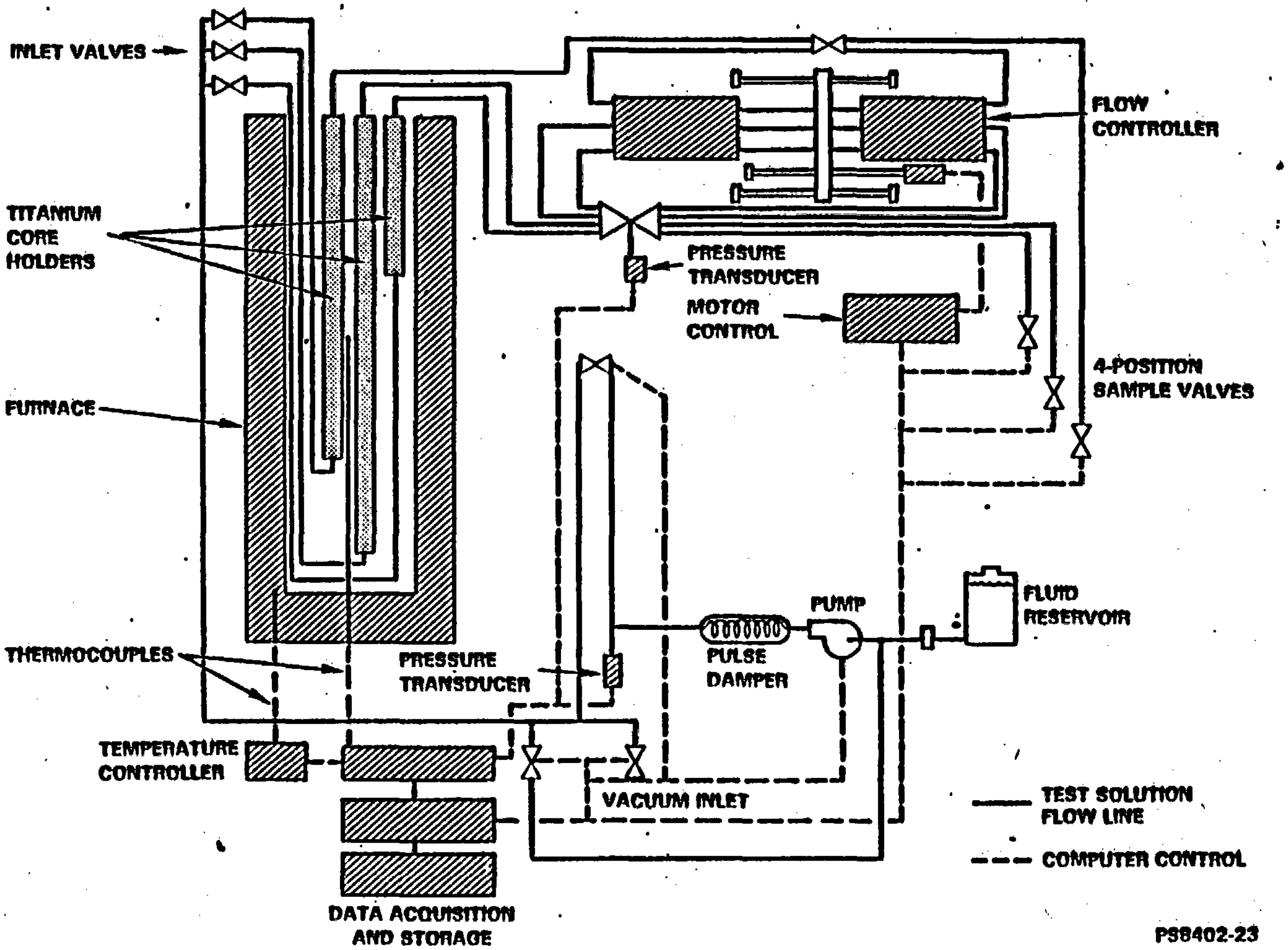


FIGURE 5-3. Schematic of Flowthrough Test Apparatus.

The pH values for samples periodically withdrawn from the autoclave during testing showed a rapid decrease from an initial value of 9.8 during the first 24-h of the experiments. After this initial decrease, the pH rose again as hydrogen ions were consumed by more rapid dissolution of primary basalt phases (Apted and Myers, 1982). The stable pH values achieved during experiments at 200°C and 300°C were 7.5 and 7.6, respectively, measured at room temperature.

The basalt particle size and water to basalt mass ratios were found to have no effect on the ultimate steady-state conditions reached during the interaction tests. They did, however, affect the length of time necessary to achieve those steady-state conditions. As expected, the only effect of using a smaller particle size as well as a lower water to basalt mass ratio waste cause steady-state conditions to be reached more rapidly.

5.1.2.1.4.2 Waste/Barrier/Rock Interactions. The early stages of barrier materials testing by the BWIP emphasized simulated waste form and simulated waste form/basalt hydrothermal tests. This approach was used because the waste form is the initial source of all radionuclides, therefore its interaction with groundwater is the primary data needed for any subsequent testing and release rate calculations. Basalt (including its secondary mineral phases), as the volumetrically dominant reactive solid within the nuclear waste repository in basalt system, is included with the waste form to study the reactions and interactions that will control radionuclide release rates in both the very-near- and near-field environments. By contrasting waste form/basalt hydrothermal test results with hydrothermal tests performed separately on waste form and on basalt, the first of several possible synergistic effects between barrier materials was studied (Apted and Myers, 1982). The results of waste form/basalt tests will, in turn, provide a baseline of information by which to evaluate tests performed on waste form/container and waste form/container/packing materials assemblages.

The use of simulated, nonradioactive waste forms for initial testing is based on the considerations of ease of handling and cost. The ease of handling of simulated, nonradioactive waste forms has enabled the BWIP to develop parallel testing activities at several laboratories, including contractual work at Arizona State University and Temple University. This has resulted in a rapid expansion of the data base for both simulated high-level waste borosilicate glass (PNL 76-68) (Ross et al., 1978) and spent fuel (Woodley et al., 1981). Many fission products produced in simulated spent fuel have nonradioactive (stable) isotopes that can be used as analogs for preparing simulated waste forms. From a chemical standpoint, the bonding interactions are essentially identical for all isotopes of the same element. It can be expected, therefore, that use of simulated, nonradioactive waste forms in testing will produce test data useful for initial performance evaluation of waste package designs where analytical sensitivity of nonradioactive isotopes is adequate.

Tests with simulated waste do not eliminate the need for testing with tracer- and high-level-doped radioactive nuclear waste forms. Many of the key radionuclides (Wood, 1980; Wood and Rai, 1981; Early et al., 1982) do not have stable isotopes (e.g., ^{99}Tc, ^{239}Pu, ^{237}Np, and ^{241}Am). The radioactivity of these key radionuclides can provide enhanced analytical sensitivity over conventional chemical analytical techniques. This is important because of the extremely low predicted solubilities of many radionuclide-bearing compounds (Early et al., 1982). Therefore, combinations of tracer-loaded and fully doped radioactive waste form/barrier/rock interaction tests are needed to:

- Test the reliability of data obtained from experiments using simulated, nonradioactive waste forms by comparison with results of experiments with tracer- and high-level-doped waste forms

- Study key radionuclides, in actual waste, that cannot be represented by stable isotopes

- Determine the effects of the expected gamma and alpha radiation fields on barrier performance

- Simulate more closely the expected condition in the repository (e.g., radiolysis).

Because many radionuclides will be released simultaneously into hydrothermal solution from actual waste forms, there is a strong probability of analytical interferences between nuclides. For example, both ^{137}Cs and ^{90}Sr are radionuclides that will be abundant in all waste form types, highly soluble in solution, and possess high specific activities. Techniques may be required to chemically separate these radionuclides from each other for radioanalysis, which is time consuming and may also introduce additional analytical errors. It is experimentally more tractable and reasonable to adopt the use of selectively doped (i.e., tracer-loaded) waste forms where feasible for testing. With waste forms such as borosilicate glass, the BWIP plans to use tracer-loaded waste forms that contain the appropriate key radionuclides identified in previous performance assessment studies (Wood, 1980; Wood and Rai, 1981; Early et al., 1982) while substituting stable isotopes, where possible, for other radionuclides so as to reduce radioanalytical interferences. Testing sponsored by the BWIP is currently underway on nonradioactive simulated spent fuel, commercial borosilicate glass (PNL 76-68 glass composition), and a simulated reference defense borosilicate glass (Frit 131) (Plodenic et al., 1982). Tracer-doped borosilicate glass (PNL 76-68 composition), with ^{99}Tc, ^{232}Np, and ^{239}Pu, has been tested with other waste package materials, starting in mid-FY 1983. A borosilicate glass (PNL 77-260 composition), selectively doped with ^{99}Tc, ^{237}Np, ^{241}Am, and ^{239}Pu, was prepared during late FY 1982 for use in both the 325 Building, 300 Area, and 222S Building, 200 West Area, hydrothermal testing programs to be started in early FY 1984. Samples of actual spent fuel (Turkey Point reactor) are currently being tested.

Waste form selection, procurement, and preparation activities are currently underway to support these hydrothermal testing programs. Testing is already underway on borosilicate glass (PNL 76-68) CHLW-form samples doped with tracer levels of ^{99}Tc, ^{237}Np, and ^{239}Pu and are described in Section 5.1.1.

Static Waste/Barrier/Rock Interaction Tests. Hydrothermal waste/barrier/rock interaction tests using static autoclaves have been performed with simulated and tracer-loaded waste forms. Similar tests with fully radioactive waste forms began on November 1, 1983, when hydrothermal testing was initiated in the hot cell test facility in the 325 Building, 300 Area. This testing is directed by the BWIP and supported by personnel from the WHC and PNL (Rockwell, 1982a).

The most recent summary of the results of testing with simulated and tracer-loaded waste forms was completed in September 1982 (Apted and Myers, 1982). Simulated spent fuel and simulated borosilicate glass waste forms were tested under hydrothermal conditions between 100° and 300°C, both alone and in the presence of Umtanum flow basalt. Steady-state solution concentrations and preliminary alteration phase identifications were made in order to evaluate specific radionuclide release rates for each waste form under site-specific test conditions.

It was found that simulated spent fuel reacts with Umtanum groundwater to produce a solution with a slightly acidic pH and higher Eh than does the same water when reacted with basalt. The groundwater/UO_2 dissolution reaction probably controls both solution pH and Eh values in the absence of basalt. The latter parameter was not measured but was interpreted as being more oxidizing than the reducing conditions that were imposed by dissolution and redox reaction of ferrous-bearing silicate glass in the basalt during hydrothermal reaction (Jacobs and Apted, 1981).

For the system-simulated spent fuel/basalt/water, steady-state concentrations for radionuclides occurring in solution were measured at 300°C and 30 MPa from stable isotopes. These concentration values were: iodine (2.2 mg/L), cesium (2.5 mg/L), rubidium (1.4 mg/L), strontium (0.7 mg/L), barium (5.0 mg/L), molybdenum (7.0 mg/L), palladium (0.1 mg/L), tellurium (0.1 mg/L), uranium (<0.05 mg/L), thorium (<0.2 mg/L), rhenium (0.7 mg/L), and samarium (0.03 mg/L). For the same system at 200°C and 30 MPa, the following steady-state concentrations were measured: iodine (4.2 mg/L), cesium (17.1 mg/L), rubidium (0.33 mg/L), strontium (0.3 mg/L), barium (≤0.5 mg/L), molybdenum (48.9 mg/L), palladium (<0.05 mg/L), and tellurium (<0.05 mg/L). Tests conducted on the same system at 100°C have yet to attain steady-state conditions after 3,000 h.

The dissolution of simulated borosilicate glass imposed a higher pH and a higher Eh than corresponding hydrothermal tests on basalt (Apted and Myers, 1982). The pH is controlled dominantly by the silicic acid buffer, although the high concentrations and unknown species of boron and molybdenum in solution make this interpretation open to further refinement. The mechanism that will prevail for buffering Eh in solution has not yet been identified for borosilicate glass, except that redox conditions are more oxidizing than those for basalt/water reactions (Apted and Myers, 1982). For the system simulated borosilicate glass/basalt/water, steady-state concentrations of radionuclides occurring in nuclear waste inventories were measured at 300°C/30 MPa from stable isotopes. These concentration values were: rubidium (10 mg/L), strontium (0.02 mg/L), barium (0.06 mg/L), and molybdenum (620 mg/L). For the same system at 200°C and 30 MPa the following steady-state concentrations were measured: rubidium (6.5 mg/L), strontium (0.02 mg/L), barium (0.07 mg/L), molybdenum (7 mg/L), and technetium (7×10^{-3} mg/L). A test performed on the same system at 100°C and 30 MPa has not reached steady-state conditions after 2,000 h.

Static-Doped Water/Barrier/Rock Interaction Tests. The performance assessment of the nuclear waste repository in basalt waste package design is concerned not only with the dissolution behavior of proposed waste forms but also in the subsequent interactions of released radionuclides with other barrier materials. These are denoted as "fate-of-radionuclides" studies and are being addressed under interaction tests using radioactively doped groundwater with barrier materials.

In these studies, a groundwater solution is used based upon the steady-state concentration values for both radioactive and stable elements found in solutions from hydrothermal tests on waste forms alone.* This new radionuclide-bearing solution represents the groundwater composition as it sequentially penetrates the barrier system during egress from the waste package. As the steady-state solution moves away from the waste form itself, it will encounter the chemically different waste package component materials and basalt. Subsequent reactions between this solution and these barriers may result in further decreases in the radionuclide concentrations in solution because of precipitation or sorption reactions. The range of possible reactions may also include the formation of highly mobile colloids that contain radionuclides (McVay and Buckwalter, 1983).

There are several advantages to these tests over static waste form/barrier/rock interaction tests. The primary advantage is that the initial solutions start with measurable concentrations of radionuclides that will only decrease with time due to reaction. This trend can be followed and documented up to the point where the solution concentration falls below conventional detection levels. In many static waste/barrier/rock interaction tests, however, the concentration of some radionuclides (or stable analogs) never rises above the detection threshold. Thus, no definitive evaluation can be made about the release of radionuclides or the capacity of the waste package barriers to mitigate release rates. Another advantage of the doped-groundwater tests is that they can reproduce, in a step-wise, barrier-by-barrier manner, the actual radionuclide reactions occurring in the outer portion of the waste package system away from the

---

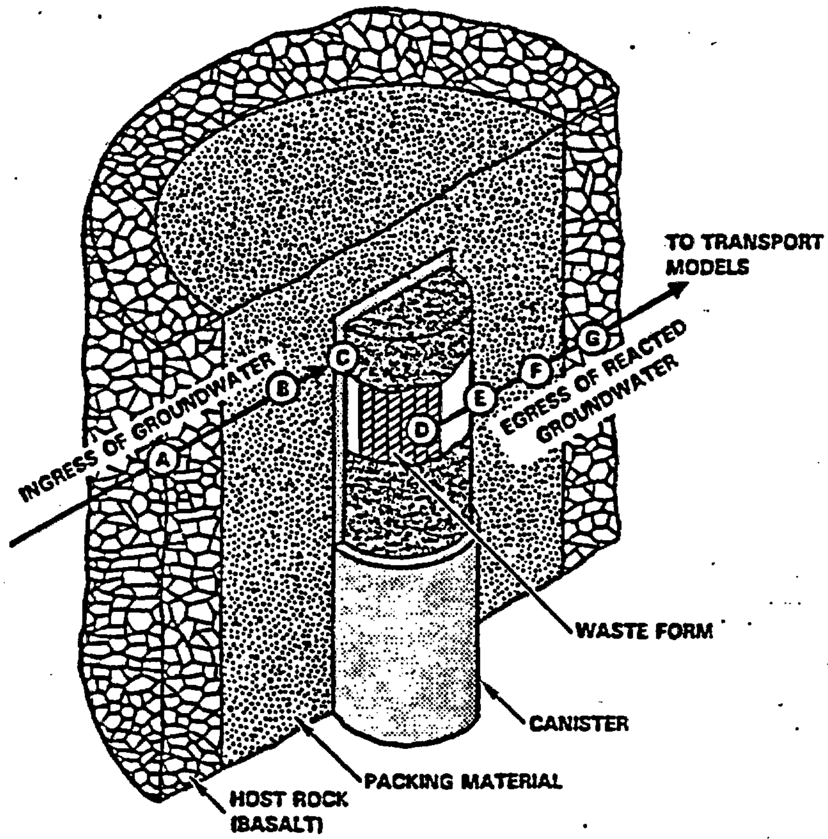
*In a similar manner, the initial groundwater used in these hydrothermal tests on waste forms is representative of ambient repository groundwater that has been chemically modified during ingress through the waste package.

waste form. A third advantage is that the results of such tests are not necessarily specific to any one waste form and can be applied to a broader interpretation of performance evaluation.

The determination of the fate of key radionuclides is currently being studied by interaction tests between radionuclide-bearing solutions and both hydrothermally altered (representative of post-1,000 yr degradation) and unaltered (representative of no degradation) barrier materials. Tests using unaltered barrier materials provide performance and design confirmation data for early release scenarios (i.e., the early period of repository history before significant basalt alteration occurs) and for release through the disturbed rock zone surrounding the waste package. Data from tests with altered packing materials and container materials are vital to the calculation of post-1,000 yr release rates from the waste package and design evaluation of potential deleterious and/or synergistic effects between barriers. Several test runs may be necessary to learn how to properly alter materials for testing.

There has been considerable work conducted previously on the sorption of radionuclides on barrier materials and basalt by the BWIP (Salter et al., 1981a; Salter et al., 1981b; Ames et al., 1982). These tests, however, utilized radionuclide concentrations that were purposefully well below the solubility limits for the specific radionuclide. Fate-of-radionuclide studies are scoped to evaluate both sorption and precipitation phenomena within the waste package. Although surface sorption is expected to be more rapid than the nucleation and growth of radionuclide-bearing solids, there is some evidence to suggest that both types of reactions will occur concurrently (Apted and Myers, 1982). In particular, the large sorption coefficients determined in several early sorption studies, using concentrated radionuclide-bearing solutions, were not due to sorption but rather resulted from the precipitation of radionuclide-containing solids.

<u>Dynamic Waste/Barrier/Rock Interaction Tests</u>. The effect of groundwater flow on hydrothermal reactions within a waste package and a nuclear waste repository in basalt has recently received theoretical (Dibble and Tiller, 1981; Dibble and Potter, 1982) as well as experimental (Relyea, 1982; Coles and Bazan, 1982; Potter, 1981; Charles and Bayhurst, 1983) treatment. The major advantage of using flowthrough autoclaves for hydrothermal testing is that the flow of water and the changes in its composition can be made to reproduce the same sequential penetration of waste form and barrier materials that occurs within the waste package (Fig. 5-4) implaced in a nuclear waste repository in basalt. This feature becomes particularly important when testing several discrete waste package components. For example, a particularly relevant test would have the water moving progressively from chemical environments dominated by the waste form, to the metal container (breached at this point), to the packing materials (presaturated to avoid swelling), and finally to the host basalt before being eluted for analysis. Data from such a scaled system test are not only used to establish radionuclide release rates as a function of flow rate but also to assess barrier compatibility. The data will indicate whether the waste package design must be altered by inclusion of additional barriers by the change of barrier materials or by the addition of special tailoring agents to the backfill to meet federal release rate performance criteria.



INTERACTIONS RELATED TO THE CONTAINMENT PERIOD	INTERACTIONS RELATED TO THE SLOW RELEASE PERIOD
A BASALT + WATER (SITE)	D WASTE + WATER (C)
B PACKING + WATER (A)	E WASTE + CANISTER + WATER (D)
C CANISTER + WATER (B)	F WASTE + CANISTER + PACKING + WATER (E)
	G WASTE + BASALT + WATER (F)

RCP8207-151B

FIGURE 5-4. Hydrothermal Interactions Resulting From Groundwater Flow Through a Waste Package.

Flow rates (linear and/or volumetric) can be changed in such testing by varying the length and diameter of flowthrough test cores, in addition to adjusting the pressure driving the flow. In this way, the effect of the flow rate on the steady-state release rate of radionuclides (Dibble and Potter, 1982; Chambre et al., 1982) can be quantified. It is currently not practical to build and operate flowthrough autoclaves that can achieve the very low-water flow rates (approximately 1 L/yr per package) measured for candidate repository horizons at the Hanford Site (Arnett et al., 1981; Gephart et al., 1979). It may be possible, however, to interpolate between the results obtained using the flowthrough autoclave and those obtained using a static autoclave in order to evaluate release rates at the low flow rates measured at the nuclear waste repository in basalt site. Flowthrough autoclaves developed from existing and successful designs (Dibble and Potter, 1982) are currently being tested by the BWIP.

A second advantage of performing flowthrough tests is that it has been demonstrated in field (Keith et al., 1978) and laboratory (Potter, 1981; Dibble and Potter, 1982) studies that flow rate can control both the reaction rate and reaction pathway in geologic systems. The principal effect of groundwater flow rates is analogous to the effect of increasing the dissolution rate of a substance in water by stirring the solution. Reaction rate constants are known to be inversely related to the thickness of the solution-solid interface boundary layer (Dibble and Tiller, 1981). This boundary layer thickness decreases with increasing flow rate. Hence, at high-flow rates the reaction rate constants increase. It may be possible, therefore, to use the control of nonthermodynamic parameters, such as flow rate or permeability, to accelerate experimental reaction rates at low temperature without causing a change in reaction mechanism. In this way, short duration tests (<2 yr) could be made to achieve a degree of reaction and alteration that is appropriate to much longer time periods.

Flowthrough hydrothermal tests have recently been performed on rock/water systems under a thermal gradient (Charles and Bayhurst, 1983; Moore et al., 1983). In addition, static rock/water tests have also been performed using a thermal gradient (Thornton and Seyfried, 1982). Enhanced mobility and mass transfer, attributed to the thermal gradient effects by these studies, have limited application to the actual conditions of a nuclear waste repository in basalt. For example, thermal gradients of 50°C/cm or more were used in these tests, while the expected maximum thermal gradient across a waste package located in basalt is 3° to 4°C/cm (Altenhofen, 1981). This maximum occurs within the first 10 yr after emplacement. A more realistic, long-term thermal gradient would be 0.1°C/cm or less. The rationale for dismissing thermal gradient effects in testing is reviewed more fully in Appendix E.

5.1.2.1.5 Planned Testing.

5.1.2.1.5.1 Basalt/Groundwater Interaction. Two hydrothermal tests in the system basalt/water are currently in progress. The first is Umtanum flow basalt/Grande Ronde Basalt groundwater at 100°C. This test will be continued for as long as necessary to determine the length of time needed to reach steady-state groundwater compositions at 100°C. The second test in progress is Cohassett flow basalt plus Grande Ronde Basalt groundwater at 150°C. This test was initiated when the Cohassett flow acquired the status of a candidate repository horizon so that the hydrothermal reaction products of this flow can be compared with that of the Umtanum flow.

The Cohassett flow contains a different proportion of mesostasis (interstitial glass) than does the Umtanum flow. During the initial stages in basalt/groundwater interactions, changes in the composition of the groundwater are controlled largely by dissolution and alteration of the mesostasis. Therefore, it is possible that the higher proportion of mesostasis in the Cohassett flow might result in a different evolution for the Cohassett flow basalt/groundwater system and influence its behavior as a repository horizon.

Planned testing includes experiments utilizing basalt from the Cohasset flow so that a comparison can be made between the hydrothermal stabilities of the Umtanum and Cohassett flows to assess the implications of a change in the repository horizon. Experiments will be conducted at 200° and 300°C, 30 MPa pressure, and a water to rock mass ratio of 10:1 using Dickson rocking autoclaves to compare the behavior of the two basalt materials. Solution analyses will be made for sodium, potassium, magnesium, calcium, fluoride, iron, manganese, aluminum, silicon, barium, chloride, SO_4^{-2}, sulfide, total dissolved carbonate, and pH. The high temperature pH of the solution will be calculated from hydrogen ion mass balance equations. Secondary phases will be characterized using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray, and other techniques. If significant differences are observed between the Umtanum flow and Cohassett flow tests, additional tests at 100°C and at other water to rock mass ratios may be required.

The entablature of the Umtanum flow is thick enough to accommodate the repository; therefore, experiments utilizing Umtanum flow basalt have been performed using material collected from the entablature of that flow. However, in the Cohassett flow, the entablature and colonnade are interlayered on a finer scale so that a repository constructed in the Cohassett flow will encompass both entablature and colonnade. Because of cooling effects, the mineralogy, proportion of glass, and the grain size differ between the colonnade and entablature of a single flow. The effects of variations in mineralogy and grain size on basalt/water interactions are not completely understood. Therefore, experiments will be undertaken using Cohassett flow basalt from both the entablature and colonnade to determine the effect of siting the repository within structural units of the Cohassett flow.

Flow Top Materials. Recent calculations indicate that, during the repository 300- to 1,000-yr containment period, the 100°C isotherm may extend into the flow top materials that lie above and below the projected repository horizon. The porosity and mineralogy of the flow tops are different from either the entablature or the colonnade, and may react differently than those materials under hydrothermal conditions. Since the flow tops may have a higher permeability than the dense interior of the flow, they may serve as groundwater conduits and may be potential pathways for radionuclide migration. Therefore, the interactions of flow top materials with simulated Grande Ronde groundwater at 100°C will be studied to determine the nature of secondary phases formed and resulting solution compositions. These data will then be used to determine the effects of hydrothermal interactions of flow tops on radionuclide migration.

The change in repository horizon, as well as additional groundwater analyses from the reference repository location, may also require a change in reference groundwater composition used in hydrothermal experiments. If a new reference groundwater is identified, experiments will be conducted to determine the validity of previous experiments that used the original groundwater formulation.

Recently, high concentrations of methane (approximately 700 mg/L) have been found in some Pasco Basin groundwaters. The presence of such a strong reducing agent in repository groundwaters might increase the rate at which the repository becomes reducing (low Eh) after decomissioning. This may alter the evolution of the basalt/water system, affecting the stability of secondary phases and radionuclide solubilities. At least one basalt/water experiment is planned that will use Grande Ronde Basalt groundwater containing 700 mg/L of methane to determine the effect of methane on the interactions.

A test also planned for FY 1984 will determine the oxygen buffering capacity of the basalt/groundwater system. This test will be performed at 200°C in Dickson-type autoclaves equipped with Teflon* hydrogen diffusion membranes. These membranes will be used to continuously monitor the partial pressure of hydrogen in equilibrium with the basalt/water system. This technique is further discussed in Section 5.1.2.4.3.

<u>Eh/pH Measurement</u>. The dissolution of the glass phase in Umtanum flow basalt and subsequent precipitation of mineral alteration phases controls both the pH and Eh of the coexisting groundwater (Jacobs and Apted, 1981; Apted and Long, 1982) at all temperatures between ambient and 300°C. The pH values measured at room temperature and extrapolated to the temperature of the experiment correspond closely with the pH values calculated for the original composition of Umtanum flow groundwater at elevated temperatures. At low temperature (<100°C), pH is controlled by silicic acid and bicarbonate buffers, while, at higher temperatures, the dissociation of water is the predominant pH buffering reaction (Apted and Long, 1982). The Eh is buffered at highly reducing conditions of approximately -400 mV at 300°C and a pH of 7.8. This value corresponds to a redox buffer interpreted to be related to the dissolution of ferrous-bearing glass, oxidation of dissolved ferrous ions to ferric ions, and subsequent precipitation of ferric oxide and silica (Jacobs and Apted, 1981). In addition, the relatively constant concentration of conservative (i.e., nonreacting) elements, such as fluoride and chloride, and the saturated concentration levels maintained with respect to such phases as silica, feldspar, and smectite clay, suggests that

*Trademark of duPont de Nemours and Company.

basalt/groundwater will recover groundwater composition, in addition to pH and Eh, under all conditions expected in a nuclear waste repository in basalt.

Several techniques are being evaluated for use in providing data on steady-state Eh and pH values, the length of time needed to achieve these steady-state values, and oxygen consumption capacity. The goal of this evaluation is to identify successful techniques for the direct and indirect measurement of the Eh conditions that exist during hydrothermal interaction tests. The following techniques and devices are under investigation:

- Measurement of dissolved redox couples such as arsenic(III)/arsenic(V)
- Direct measurement of dissolved oxygen levels
- The use of a redox-sensitive pair of solid phases such as cobalt-cobalt oxide or magnetite-hematite encapsulated in a metallic or Teflon hydrogen diffusion membrane
- The use of a Teflon hydrogen diffusion membrane installed within the autoclave and connected to an external pressure gauge
- The use of electrochemical Eh sensors
- The use of zirconia pH sensors.

The dissolved redox couple and the solid phase redox-sensing capsules will set limits or bracket Eh conditions. The direct measurement of O_2 and H_2 levels utilizes analytical techniques that can be performed on samples periodically withdrawn from the autoclave during the test. The Teflon H_2 diffusion membrane and the electrochemical Eh sensor are designed to provide continuous real-time data on the Eh conditions existing during the test by inserting them through the autoclave top into the test solution. The zirconia pH sensor will also be able to provide continuous monitoring of pH conditions in the same manner. The following subsections described the Eh/pH measuring techniques being evaluated.

<u>Measurement of Dissolved Redox Couples</u>. Cherry et al. (1979) introduced the concept of using measured concentrations of arsenic(III) and arsenic(V) species to compute apparent redox conditions in groundwater. Very low arsenic concentrations (1 to 10 µg/L) can be detected due to the analytical capabilities of hydride generation-Atomic Absorption Spectroscopy (Shaikh and Tallman, 1978). Arsenic(III) and total arsenic are determined independently by Atomic Absorption Spectroscopy, arsenic(V) is determined by difference, and the arsenic(III)/arsenic(V) ratio is then calculated. Laboratory tests conducted by Cherry et al. (1979) suggest that redox reactions of arsenic species in natural waters occur at rates sufficiently slow at room temperature to enable samples to be collected and analyzed before significant changes in the arsenic(III)/arsenic(V) ratio take place.

The arsenic speciation technique developed by Cherry et al. (1979) has been modified to evaluate the redox conditions developed during basalt/water hydrothermal experiments (Lane et al., 1983). If starting solutions are spiked with trace levels of arsenic(V), then subsequent arsenic oxidation state analysis would provide the basis for estimating the solution Eh developed during the experiment. This technique is currently being used successfully to estimate Eh conditions at hydrothermal test temperatures.

Dissolved Oxygen Measurements. Measuring the dissolved oxygen content of solution samples periodically withdrawn from autoclave tests is a direct method of investigating oxygen consumption in the basalt/groundwater system. However, this approach has several experimental and analytical difficulties. Contamination from atmospheric oxygen during sampling and analysis is difficult to avoid. In addition, there are potentially numerous chemical interferences that may exist during analysis. The major drawback to this technique is that the lower limit of detection is in the range of several parts per billion dissolved oxygen. This lower limit of detection still represents moderately oxidizing conditions relative to those imposed by the basalt/water interactions in a nuclear waste repository in basalt. However, this technique can be useful, especially when coupled with other techniques more sensitive in the reducing range, to establish a rate of approach to equilibrium conditions.

The American Public Health Association (1976) and the EPA (1979) recognize two methods for dissolved oxygen analysis: (1) the Winkler or iodometric titration and (2) the electrimetric method using membranes electrodes. Gilbert et al. (1982) compared dissolved oxygen measurements of distilled water by the Winkler method and by membrane electrode. The two methods gave essentially the same results within their uncertainties ($\leq$0.2 mg/L). One of the standard methods for dissolved oxygen in water, described by the American Society for Testing and Materials (ASTM, 1976), is a colorimetric technique using indigo carmine. CHEMetrics, Inc. sells test kits for colorimetric analysis of dissolved oxygen using indigo carmine and rhodazine D reagents. Several successful dissolved oxygen measurements of solutions from the basalt/water hydrothermal experiment were made by the BWIP using the CHEMetrics kits. Also, Gilbert et al. (1982) compared the CHEMetrics indigo carmine colorimetric technique with dissolved oxygen measurements made with a membrane electrode. Several natural waters were tested and the two methods gave comparable results ($\leq$0.5 mg/L difference at dissolved oxygen concentration of 7 mg/L).

Oxygen depletion studies were completed by the BWIP using both membrane electrodes and colorimetric techniques; both yielded similar results (Lane et al., 1983). The dissolved oxygen content of solutions measured at room temperatures, withdrawn from hydrothermal tests in which basalt was reacted with synthetic Grande Ronde Basalt groundwater at 150°C, decreased from air saturated solutions (8-9 mg/L) to 0.4 mg/L after 8 days exposure. Solutions from a similar experiment conducted at 100°C contained <2 mg/L after 130 days.

Commercial dissolved oxygen analyzers employ a Clark-type membrane-covered polarographic sensor. The sensor consists of a platinum cathode and a silver anode in a potassium chloride solution. The gas-permeable membrane is Teflon and is designed to separate the electrolytic cell from the sample to avoid poisoning and changes in electrolyte composition. The cell reactions can be written (Phelan et al., 1982):

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad \text{(cathode)} \qquad (1)$$

$$H_2O + 2Ag = Ag_2O + 2H^+ + 2e^- \qquad \text{(anode)} \qquad (2)$$

$$O_2 + 2Ag = Ag_2O \qquad \text{(overall)} \qquad (3)$$

Under steady-state conditions, the current in the oxygen sensor is directly proportional to the activity of molecular oxygen. The effects of chemical interferences can be reduced by calibrating the dissolved oxygen meter using air saturated water of the same composition and at the same temperature as the groundwater to be measured.

Redox Sensing Solid Phases. A two-phase solid assemblage of a metal and its oxide can be used as a simple redox indicator. An assemblage such as cobalt - cobalt oxide, at any given temperature, pressure, and pH, is only stable at a unique Eh value. If the Eh is above this value, the metallic cobalt will oxidize, and, if the Eh is below this value, the oxide phase will reduce. In an aqueous environment the reaction can be written:

$$Co + H_2O = CoO + H_2 \qquad (4)$$

The assemblage must be isolated from the test system so that it does not contaminate the test solution. This can be done effectively by sealing the assemblage-groundwater in an inert capsule that has a high hydrogen diffusivity, such as platinum or palladium. The hydrogen fugacity (f_{H_2}) established by the system being tested will fix the f_{H_2} inside the sensor capsule. This will cause either an oxidation or reduction of the assemblage, depending on the f_{H_2} value. At the conclusion of the experiment, the capsule can be split open and X-rayed to determine if the assemblage has oxidized or reduced.

The sensor capsule can only be retrieved by terminating the test; therefore, this technique will only provide information on the Eh conditions achieved at the end of the test. A further limitation to this technique is that a single assemblage will establish a limit on the redox conditions; that is, the Eh was above or below a certain value. It would be necessary, therefore, to employ several different assemblages in separate capsules so that the Eh conditions can be bracketed. To be useful, an assemblage must react to changes in f_{H_2} rapidly at the temperature of interest and must have an equilibrium f_{H_2} value within the range of interest. Some possibly useful assemblages are listed below along with their equilibrium log f_{O_2} values calculated at 300°C and 30 MPa:

Assemblage	Equilibrium Log fO_2
Co-CoO	-35.1
$Cu-Cu_2O$	-22.8
Ni-NiO	-34.1
$MnO-Mn_3O_4$	-29.0

A potential problem in the use of a sensor capsule such as this in Dickson rocking autoclaves is that the sensor capsule may be abraded by the rocking motion. An experiment performed at ambient temperature and 0.1 MPa pressure, containing a platinum capsule loaded with a buffer assemblage plus water, was conducted by Temple University (under contract to the BWIP) to evaluate the possibility of abrasion. There was obvious abrasion of the platinum capsule, but the abrasion was mostly localized to the fin-like closure areas and the edges of the body. This would indicate that the capsule was rubbing against the gold bag rather than being abraded by the basalt, but there were no visible signs of abrasion on the gold bag. The capsule was weighed before and after the experiment; however, a small hole in the capsule allowed water to enter, causing irreversible hydration of the buffer. As a result, the capsule gained weight, and no quantitative estimate of the abrasion rate could be made. Due to the lack of visible abrasion it is believed that the capsule would probably survive a long duration experiment, particularly if the rate of rocking could be decreased.

Sensor capsules are currently in the process of being tested at Temple University, under contract to the BWIP, by incorporating capsules into ongoing basalt/water and basalt/waste form/water interaction tests. If successful, this technique can be used to bracket the final Eh conditions reached during the test, and, coupled with other techniques, can be used to determine the rate of approach to the final Eh conditions.

Teflon Hydrogen Diffusion Membrane. The H_2 content of the hydrothermal solution can be continuously monitored by incorporating a hydrogen diffusion membrane within the autoclave. One surface of the membrane is in contact with the solution to be investigated, and the other side of the membrane is connected to a pressure transducer. If the membrane allows H_2 to diffuse and if this diffusion occurs at a fast enough rate, the pressure measured at the transducer will equal the f_{H_2} of the solution and the Eh can be calculated.

Teflon, a fluorocarbon polymer, is well known for its chemical inertness, its thermal stability at temperatures up to 390°C, and its excellent electrical insulating properties. However, it does degrade at a gamma dose above 10^8 R which may limit the use of this measurement technique to tracer-doped testing. It is unaffected by most inorganic and many organic compounds. Teflon also exhibits a relatively large hydrogen gas permissivity; therefore, it has potential as a selective osmotic membrane for hydrogen.

The Arizona State University Chemistry Department, under contract to the BWIP, has designed an H_2 diffusion membrane consisting of a 3-in.-long, 1/4-in.-OD, closed-end, Teflon tube with a wall thickness of 0.03 in. The mechanical strength of the membrane was tested to 260°C and 33.8 MPa. It was able to withstand fluid pressures and pass H_2 under these conditions. Calibration experiments were carried out in a static modified Dickson autoclave to test the efficiency of the Teflon membrane and to calibrate the membrane against known solid-solid f_{O_2} buffer reactions. The reactions investigated were:

$$Co + H_2O = CoO + H_2 \tag{5}$$

and

$$3Fe + 4\ H_2O = Fe_3O_4 + 4H_2 \tag{6}$$

The results of the calibration experiments indicate that the experimentally measured hydrogen pressure induced by basalt/water interactions reaches values that are within the experimental uncertainty of the values predicted from available thermodynamic data. The diffusion of gaseous components other than H_2 (such as CO_2, H_2O, SO_2, H_2S, or CH_4) through the membrane could potentially introduce errors in the measurements, since these components will contribute to the total pressure as measured by the transducer. However, the use of a liquid nitrogen cold trap installed in the pressure line between the diffusion membrane and the pressure transducer could be used to condense all possible gases that may cause interferences in the hydrogen measurement. An alternative technique would be to remove a small volume of the gas and analyze it using gas chromatography to determine the partial pressures of the various gas components present. From these data, the partial pressure of hydrogen in equilibrium with the system being tested could be determined, which would allow the Eh to be calculated.

Basalt/water interaction tests, performed in Dickson autoclaves equipped with Teflon hydrogen diffusion membranes, are currently planned at Temple University. Preliminary results indicate that Teflon membranes appear to effectively provide accurate, continuous monitoring of the partial pressure of hydrogen in equilibrium with the system being tested.

Electrochemical Eh Sensors. The current design for an in situ electrochemical Eh sensor consists of a 1/16-in.-diameter, inert, metal wire that would penetrate the Dickson autoclave head through a Conax pressure/electrical fitting. Various candidate electrode materials were autoclave tested as a function of temperature, pH, and Eh to determine the speed and stability, the chemical inertness, and the thermodynamic reversibility of the Eh response. Platinum, gold, and titanium were tested simultaneously in a multiport autoclave. Platinum was determined to be the best metal for use under hydrothermal conditions (Danielson et al., 1983). The use of a platinum Eh electrode necessitates the use of some type of reference electrode to complete the circuit. Several reference electrode designs will be tested during FY 1984.

pH Probes. The design of a zirçonia (ZrO_2) pH sensor being evaluated for use with an autoclave is based on a recent discovery by Niedrach (1980) that ZrO_2 stabilized with 8 mol% yttria (Y_2O_3) will develop an electrical potential across its surface, which is proportional to the difference in the pH of the solutions contacting its surfaces. The stabilized ceramic material is in the form of a sintered closed-end tube that will penetrate through the autoclave head so that the outer wall of the tube is in contact with the test solution. The inner electrode is composed of a mixture of copper and copper oxide (Cu_2O) surrounding a copper wire that passes through the autoclave head and is connected to a high-impedance electrometer. The circuit is completed by employing a separate reference electrode that is also connected to the electrometer.

5.1.2.1.5.2 Waste/Barrier/Rock Interaction.

Waste Forms. The testing of simulated waste forms was concluded at the end of FY 1983. The focus of waste form testing now shifts to tracer-loaded and fully radioactive waste forms. The BWIP waste/barrier/rock interactions testing program will encompass a broad range of waste types (i.e., spent LWR fuel, DHLW borosilicate glass, CHLW incorporated in either borosilicate glass and/or crystalline ceramic material, and CHTRU wastes incorporated in either glass, cement, or tested as-is). The concentration of radionuclides present in these waste form(s) will cover the range from simulated, non-radioactive waste forms to fully radioactive waste forms and spent fuel. An important part of this range of waste form sample materials will be those that are selectively doped with key fission products and/or actinides up to concentration levels optimized for radiochemical analysis or up to the actual levels in a fully radioactive waste form.

Reference waste forms and additional alternate, second generation waste forms will be tested as directed by the DOE, contingent upon the delivery of samples from the responsible commercial and defense waste form programs.

Static Waste/Barrier/Rock Interaction Tests. There are several separate subtasks within the scope of static waste/barrier/rock interaction tests. These are distinguished by different types of waste forms (CHLW versus DHLW) and different degrees of radionuclide loading (simulated versus tracer-loaded versus fully radioactive). Each subtask will be reviewed separately in the following text.

<u>Simulated Commercial High-Level Waste</u>. This subtask is in its final stages of testing activity. Data have been collected on simulated spent fuel (Woodley et al., 1981) and simulated PNL 76-68 borosilicate glass (Ross et al., 1978) both alone and in the presence of basalt. A series of tests were performed at temperatures from 100° to 300°C and a variety of water to solid mass ratios and surface area to volume ratios. The most recent summary of steady-state concentration data and identification of radionuclide-bearing alteration solids was documented by Apted and Myers (1982) and Myers et al. (1983). Work on this subtask was completed by the end of FY 1983, in order to support performance analyses of the Waste Package Advanced Conceptual Design.

<u>Tracer-Loaded and Fully Radioactive Commercial High-Level and Transuranic Waste</u>. A joint effort, directed by the BWIP and involving the PNL and the WHC, was initiated in early FY 1984 for developing and performing hydrothermal tests utilizing tracer-loaded and fully radioactive waste forms in a hot cell test facility at the 325 Building, 300 Area. Tests using barrier materials in the presence of these waste forms under static conditions were initiated in November 1983 in this facility. Hot cell testing of waste package components with fully radioactive waste forms is considered vital for:

- Measuring steady-state concentrations, hence release rates, of key radionuclides from waste forms
- Identifying radionuclide-bearing hydrothermal alteration phases, which will impose long-term solubility limits that, in turn, determine radionuclide releases from the waste form and waste package
- Evaluating the effect of radiation fields on waste package degradation and radionuclide release rates from the waste package
- Establishing synergistic effects of other barrier materials on waste package degradation and radionuclide release from the waste package.

Specific data to be obtained from use of fully radioactive waste forms were listed as to Data Categories 1 through 7 in Table 5-4. The direct applications of these data to performance assessment and waste package design are also listed in Table 5-4 and discussed in subsequent sections. Defensible performance assessment relies on conformance testing of the waste package that can reproducibly demonstrate that acceptable slow release of radionuclides (NRC, 1982) can be attained. Computational models for waste package and repository safety assessment are predicted on actual, verifiable test data for radionuclide concentrations in groundwater.

Waste/barrier/rock interaction tests will be performed for each of several tracer-loaded and fully radioactive waste forms. Reference waste forms to be tested will include commercial borosilicate glass, spent fuel, and TRU wastes. Because of the low temperatures (90°C and 150°C) of these tests, test durations of 12 months may be required to reach steady-state radionuclide concentrations. These time-independent concentrations will aid performance assessment of the waste package by confirming radionuclide solubility limits and hence release rates. These tests will provide the key data required to complete and confirm the performance analysis of the waste-package preliminary design.

During FY 1984, hydrothermal testing will center on waste form and waste form/basalt (backfill) testing. Evaluation of the analytical difficulties in measuring groundwater solutions reacted with fully radioactive waste forms will be made, and radionuclide separation techniques will be perfected. Testing in FY 1985 will include waste form, waste form/container, and waste form/container/packing materials tests. Through FY 1986 and FY 1987, testing will focus extensively on waste/container/backfill tests. Comparisons will be made between the solubility/steady-state concentrations obtained in tracer-loaded waste form tests and those conducted under the same run conditions but using fully radioactive waste forms. These comparisons will indicate if data obtained from the lower radiation-field tests resulting from the use of tracer-loaded waste can be used to assess the radionuclide release behavior of fully radioactive waste forms and associated higher radiation fields. Because of the ease of operation and reduced analytical difficulties, it would be preferable if selectively doped tracer-loaded waste forms could be used for the bulk of the testing. The use of a radiation field here should not be confused with the use of a high intensity gamma source to measure the effects of radiation on corrosion described in Section 5.1.2.3.5.2.

Defense High-Level Waste. The BWIP Engineered Barriers Department is currently engaged in a joint waste form testing activity with Savannah River Laboratory. The Savannah River Laboratory is the lead organization for the development and fabrication of DHLW forms. The joint BWIP-Savannah River Laboratory test program is to determine the ability of the Savannah River Laboratory DHLW form, a borosilicate glass (Plodenic et al., 1982), to meet proposed federal nuclear waste containment criteria for a nuclear waste repository in basalt (NRC, 1983a). The data to be collected are needed to confirm the solubility-limited radionuclide release rates of Savannah River Laboratory glass under expected repository conditions.

Phase One tests of this joint program were initiated in December 1982 by the BWIP. The effort involves testing of simulated, nonradioactive (uranium-free) Savannah River Laboratory borosilicate glass, alone and in the presence of basalt, at 90° and 150°C. Phase Two of testing will involve waste form/barrier/rock interaction tests at 90°, 150°, and 200°C. The scheduled startup of the Savannah River Laboratory portion of Phase One tests is currently awaiting the development of site-specific testing procedures by Savannah River Laboratory. The Savannah River Laboratory procedure for testing involves modification of an existing Materials Characterization Center MCC-1 procedure (MCC, 1981), mainly by the substitution of machined basalt cores for the reaction vessel. Data obtained by both the BWIP and Savannah River Laboratory during Phase One will be collated by the BWIP for evaluation. Phase One test results will be used to determine preliminary waste form release rates to support the preparation of the "Waste Form Acceptance Requirements and Specifications," a draft of which has been completed and reviewed. Phase One testing will continue into FY 1984, using tracer-loaded defense glass to further evaluate waste form release rates. Phase Two testing will be initiated at the end of Phase One, by the end of FY 1984. The scope of testing for Phase Two is currently under discussion and revision.

Materials Characterization Center. The BWIP Waste Package Program is working in conjunction with the Materials Characterization Center to develop procedures for a low-temperature, repository-specific, radionuclide release test for acceptance testing of waste forms in the presence of other barrier materials (MCC-14). The MCC-14 test procedure will provide a useful comparison to other test methodologies for barrier material testing, including the BWIP reference test procedures using Dickson-type sampling autoclaves as outlined in previous sections. These tests are designed to determine a waste package release rates based on steady-state/solubility limits to release at expected nuclear waste repository in basalt temperatures and pressures. This new test (MCC-14) is oriented toward producing defensible solubility/steady-state data on radionuclides rather than data on mechanistic studies of waste form dissolution. It is expected that data from these tests will complement the primary Dickson autoclave test methodology used by the BWIP in performing waste package studies.

The Materials Characterization Center is developing the MCC-14 test based on equipment, test procedures, reference materials, and monitored experimental parameters agreed to by the BWIP Engineered Barriers Department. This preliminary work by the Materials Characterization Center was completed in FY 1983. The BWIP has directed the Materials Characterization Center to include complete solution analysis for cations and anions, as well as pH in MCC-14. The Eh in sampled solutions also must be monitored or estimated indirectly by means of dissolved redox sensitive couples. Associated radionuclide-bearing alteration solids and any potential colloidal material formed during the MCC-14 tests must be characterized by the appropriate analytical techniques, including analytical scanning transmission electron microscopy. In subsequent years, this specific test method (MCC-14) will be tested and evaluated by the Materials Characterization Center against the existing BWIP static testing methods.

During FY 1984 the emphasis of the Materials Characterization Center test development activities being done for the BWIP is devoted to designing a compliance test for evaluating candidate waste form systems relative to the acceptance requirements (specifications) being developed by the BWIP on radionuclide release from such systems. Both a procedure and a test system are being developed. The test system and procedure are meant to provide a relatively simple means for obtaining performance data on candidate waste form system materials. These data will then be used to judge whether the subject material system does or does not meet the requirements (specifications) set by the BWIP for acceptance of materials for disposal in the repository. An integral part of the final development of such a compliance test will be to demonstrate the intercomparability of the data obtained, using it and the overall data base generated by the BWIP in support of a repository system license. See Section 5.1.1.1.4.4 for further discussion of the preparation of waste form system acceptance requirements and specifications.

Static-Doped Water/Barrier/Rock Interaction Tests. During FY 1984, fate-of-radionuclide studies implemented by the BWIP will include examination of chemical reactions that will affect transport of radionuclide-contaminated water through waste package barrier components. These studies will require measurement of the extent and rate of reactions of key radionuclides with unaltered and hydrothermally altered barrier materials. Specifically, both sorption and precipitation reactions of radionuclides will be identified and quantified by determining sorption isotherms for each of the key radionuclides. Solubilities of these radionuclides will be estimated from isotherm measurements, which will be extended to high radionuclide concentrations. Both solubility and sorption will be measured over a range of important environmental parameters (Eh, solution composition, time, solid/solution ratio, and temperature). The ranges of variables will be those expected in the waste package components during release of the radionuclides.

The reversibility of radionuclide sorption on barrier materials must also be measured during FY 1983 and FY 1984 tests in order to accurately model transport of radionuclides through the barriers. Sorption reversibility will be determined by measuring increases in radionuclide concentrations in nondoped hydrothermal solutions that are contacted with tracer-loaded barrier material. This desorption will also be measured over a range of significant environmental parameters. Testing during FY 1985 and FY 1986 will include radionuclide reactions with altered container material (corrosion product) and basalt. Canister corrosion products are likely to include iron oxides and hydroxides and possibly sulfides. These substances are known to sorb some radionuclides very strongly. Therefore, formation of radionuclide-bearing colloids from barrier hydrothermal alteration may be a significant factor in radionuclide transport through waste package barrier materials, requiring design modification in the composition or structure of proposed barriers. A variety of altered packing materials and container materials will be studied to determine their stability and their influence on radionuclide release rates under conditions simulating those expected in a nuclear waste repository in basalt.

The identification of solid products of hydrothermal reactions is an important part of the rate-of-radionuclide studies. Identification of those solid phases containing the radionuclides will complement the information obtained from analyses of solutions. Electron beam techniques (scanning electron microscope, scanning transmission electron microscope, microprobe, etc.) will be used to identify the solid phases. Of particular importance are solid phases that control the solubility of radionuclides (see Appendix B). Results observed in these tests will be compared to those obtained from static and dynamic waste/barrier/rock interaction hydrothermal tests.

Dynamic Waste/Barrier/Rock Interaction Tests. A flowthrough autoclave system, with three independent flow columns, was delivered to the BWIP in mid-FY 1983. Dynamic tests are needed to simulate radionuclide transport and reaction through a waste package configuration. Dynamic test results will help to confirm or bracket actual radionuclide release rates based upon static test data. Furthermore, by controlling flow rate, it may be possible to accelerate reaction rates, which in turn could validate the use of short-term (<1 yr) laboratory data for long-term (>100 yr) predictive modeling.

Initial tests will concentrate on evaluating flow rate effects on steady-state concentrations and formation of alteration solids in the systems basalt and basalt/tracer-loaded waste forms. Flowthrough tests on the assembled components of the waste package using tracer-loaded waste will be conducted in mid-FY 1984. Because of the importance of flowthrough testing, a second flowthrough autoclave system is to be procured in early FY 1984, specifically for testing with fully radioactive nuclear waste forms. During FY 1984, one flowthrough system will be used exclusively for determining the release rate of radionuclides from a waste form plus container. The second flowthrough system will be used to measure release rates as a function of flow in the system waste form/backfill* during this same period. Both commercial and defense reference borosilicate glass, doped with appropriate key radionuclides (see Table 4-1), will be used. During FY 1985, flowthrough tests will begin to use fully radioactive waste forms to compare release rates to similar tests performed with tracer-loaded waste forms.

Actual spent fuel will be included in these tests. During FY 1986 and FY 1987, final system conformance tests will be performed on scaled versions of the preliminary BWIP waste package design. These will include assembling the various waste form, container, backfill, and basalt barriers in the hot cell. In addition to demonstrating acceptable radionuclide release rates, examination of alteration products will serve to establish alteration solids controlling the long-term release of radionuclides, as well as any synergistic effects on release rate rising from inter-barrier reactions. These tests represent the final radionuclide release rate testing for the preliminary waste package design.

The hydrothermal gradient across an emplaced waste package has been calculated to be small and is expected to have little effect on mass transport under hydrothermal conditions. A review of thermal gradient effects is contained in Appendix E.

---

*Because of the intended swelling properties of reference backfill materials (Anderson, 1982), it will not be possible to sustain a saturated flow through a column of backfill. Substitution of crushed basalt alone will be used to approximate the role of backfill, which is 75% basalt and 25% bentonite.

5.1.2.1.6 Logic Diagram. The waste/barrier/rock interactions data required to support waste package design and performance assessment must be generated in a manner consistent with the design and performance assessment schedules. A logic diagram showing the relationship between the waste/barrier/rock interactions studies and input to the design and performance assessment efforts is presented in Figure 5-5 and 5-6.

5.1.2.2 Near-Field Geochemistry

5.1.2.2.1 Introduction. This section describes the laboratory testing activities required for determining the sorption and solubility behavior of radionuclides released from a breached container to the repository horizon. The repository horizon is defined as the basalt flow containing the engineered barrier systems (excluding flow tops and interbeds). Solubility control and sorption, which may be active in all segments of the waste isolation system, represent potentially important mechanisms for retarding the migration rate of radionuclides from the engineered barrier system. Precipitation of stable, radionuclide-bearing phases establishes control of the maximum concentration of each radionuclide dissolved in groundwater (solubility limit). Sorption of dissolved radionuclides on solid materials in the flow path will determine radionuclide concentrations along the flow path. In addition to migration in true solution, transport of radionuclides in colloidal or particulate form may occur and must be evaluated.

Radionuclide solubility and sorption behavior is highly dependent on the environmental conditions of the repository horizon. Temperature, pH, Eh, radiation field, groundwater composition, the composition of hydrothermally altered waste package materials, basalt fissures, and disturbed rock zone, in particular, are important factors that can control radionuclide solubility and sorption behavior. In addition, the physical and chemical characteristics of the geologic substrate along postulated flow paths are important factors in evaluating radionuclide retardation behavior. The environmental conditions expected for a nuclear waste repository in basalt are discussed in detail in the BWIP Site Characterization Plan.

Preliminary radionuclide release modeling using the best estimates for critical parameters (based on work in progress at the BWIP), including sorption coefficients and solubilities, have resulted in the compilation of a list of key radionuclides (Table 5-6) for which predicted releases from the waste package or to the accessible environment may exceed NRC or EPA criteria, respectively (EPA, 1982; NRC, 1983a). The identification of key radionuclides is most important to the BWIP experimental program in that it guides future solubility and sorption studies to those nuclides for which release criteria are most stringent.

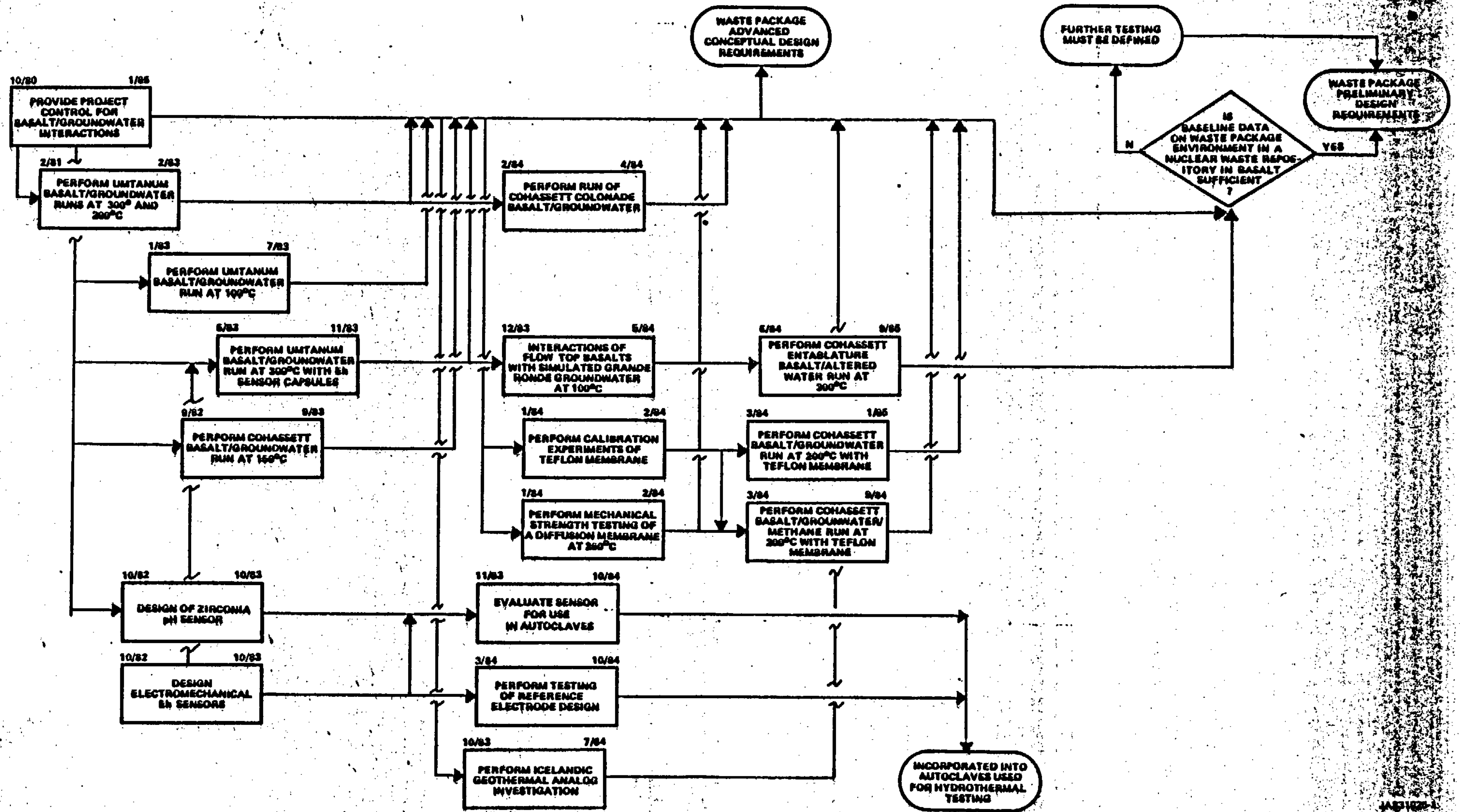


FIGURE 5-5. Basalt/Groundwater Testing Logic Diagram.

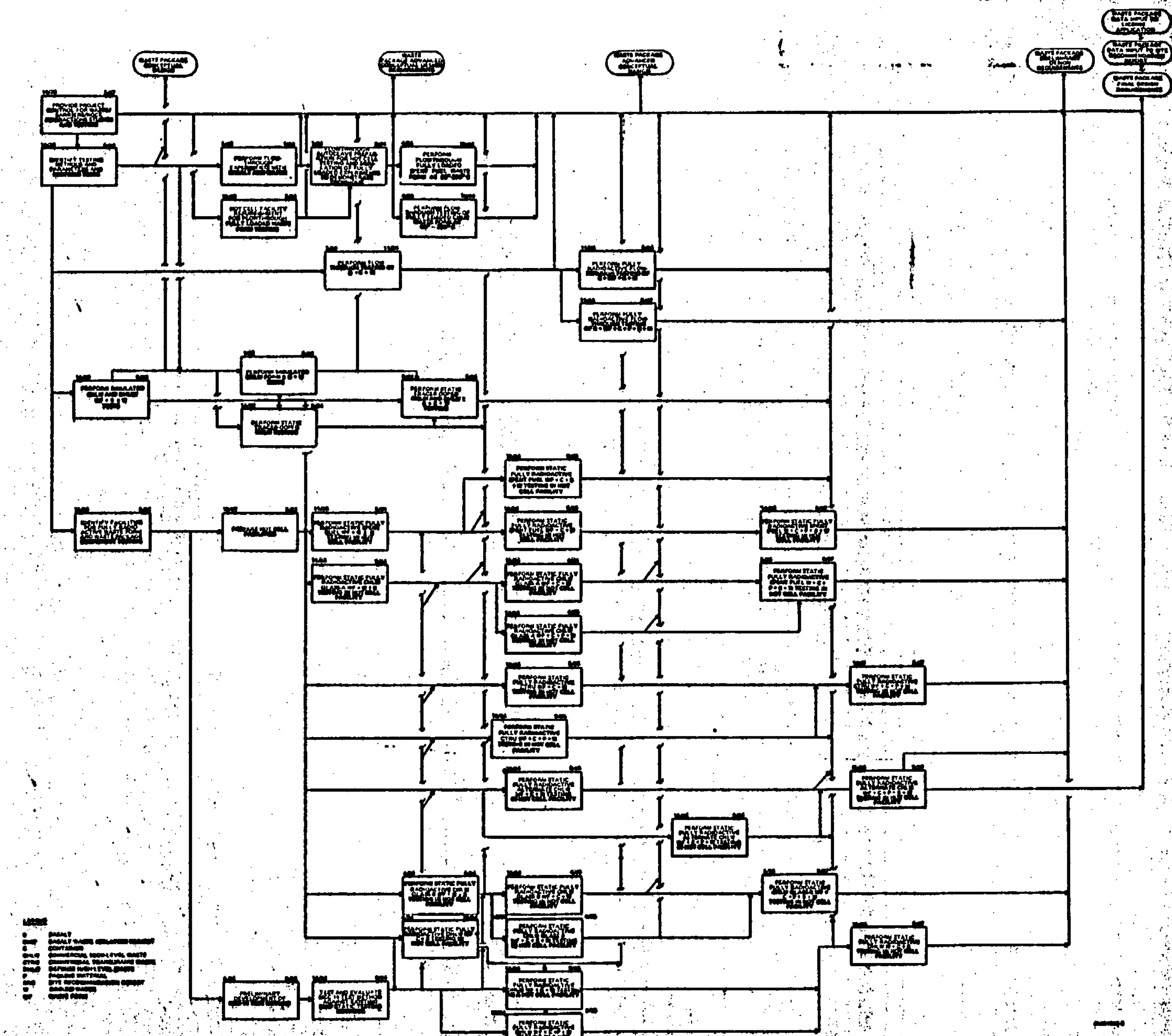


FIGURE 5-6. Waste/Barrier/Rock Interactions Testing Logic Diagram.

TABLE 5-6. Preliminary List of Key Radionuclides for a Nuclear Waste Repository in Basalt. (100-yr-old Commercial High-Level Waste or Spent Fuel)

Element	Radionuclide	
	Priority 1	Priority 2
Carbon	^{14}C[a]	
Iodine	^{129}I[a]	
Selenium	^{29}Se	
Technetium	^{99}Tc	
Neptunium	^{237}Np	
Plutonium	^{239}Pu, ^{242}Pu	^{238}Pu, ^{240}Pu, ^{241}Pu
Tin	^{126}Sn	
Strontium		^{90}Sr[b]
Cesium		^{135}Cs, ^{137}Cs[b]
Radium		^{226}Ra[b]
Curium		^{243}Cm, ^{245}Cm, ^{246}Cm
Protactinium		^{231}Pa
Nickel		^{59}Ni, ^{63}Ni
Uranium		^{233}U, ^{234}U, ^{235}U
Lead		^{210}Pb
Zirconium		^{93}Zr
Palladium		^{107}Pd
Thorium		^{229}Th, ^{230}Th, ^{232}Th
Americium		^{241}Am, ^{243}Am

[a]Spent fuel only.
[b]Existing data sufficient.

The list of radionuclides in Table 5-6 was derived by considering the total inventory in the 100-yr-old waste forms. Those with a half-life of <20 yr were rejected. Of the remaining, those with an inventory of <0.1% of the EPA limit were rejected. A preliminary transport analysis of the remaining radionuclides using conservative hydrologic properties, sorption, and solubilities values was then completed on those remaining. The ones that appeared to exceed 0.1% of the EPA limit at the accessible environment were prioritized for Table 5-6. Priority 1 includes those radionuclides with solubility or sorption characteristics that must be well understood to assure isolation performance. Priority 2 includes those radionuclides with solubility or sorption characteristics that require confirmatory data to determine their impact on isolation performance. This list of radionuclides is preliminary and is continually under review by the BWIP and may be modified in the future..

5.1.2.2.2 Objective and Justification. The objective of these studies is to provide sufficient data on radionuclide solubility, sorption, and colloid formation to allow reliable prediction of radionuclide release and transport in the repository horizon, including the waste package material. This information will be incorporated into radionuclide transport models that partially determine the design requirements for the engineered barrier system and that predict the performance of the engineered barriers system and the portion of the geologic setting that provides isolation.

Radionuclide transport by groundwater intrusion into the waste package, and subsequent dissolution of the waste form from a failed container and migration through the repository horizon, is the most probable mechanism that could lead to radionuclide release to the accessible environment. Sorption of dissolved radionuclides onto solid engineered materials or geologic materials is an important mechanism for preventing or retarding radionuclide transport. In the repository horizon, sorption of released radionuclides can occur on corroded container material, hydrothermally altered packing materials and backfill material, hydrothermally altered basalt, colloids, or on minerals lining fissures in the basalt rock mass surrounding the repository. Radionuclide transport in groundwater, after the waste containers are breached, is partially controlled by sorption on these materials.

The solubility of key radionuclides will control their release to the groundwater and define the maximum radionuclide concentrations in groundwater. Solubility reactions may be most important in the packing materials or even on the surface on the waste form itself. However, as with sorption, the BWIP must examine experimentally how well radionuclide solubility in each component of the engineered barrier system limits the release of radionuclides to the accessible environment.

Mass transport by colloid particulates represents a mechanism that may lead to enhanced transport of radionuclides. Radionuclide sorption on colloids may be important if the colloids can be transported by convective groundwater flow or diffusion from the repository. Colloids can be classified as either true or pseudocolloids. True colloids can form in a solution that is supersaturated with respect to an insoluble phase containing a radionuclide as an essential component. Hydroxides and hydrated oxides are common chemical forms for true colloids of many radionuclides (Apps et al., 1983). Pseudocolloids commonly are clay, silica, or iron hydroxide particulates to which radionuclides can sorb. These pseudocolloids might be generated by degradation of engineered barrier system components or by precipitation of groundwater components. Because of this potential transport mechanism, it is important to investigate the conditions of colloid formation, their stability in the basalt geochemical system, and their ability to migrate through the components of the engineered barriers system.

Models of radionuclide transport in groundwater require input of laboratory sorption, solubility, and colloid formation data to accurately predict transport rates and radionuclide concentrations in groundwaters.

5.1.2.2.3 Summary of Data Needs.

5.1.2.2.3.1 Sorption and Colloids Testing. Table 5-7 summarizes the data needed to complete radionuclide sorption testing. Site-specific engineered barrier materials (container and packing materials and backfill), geologic materials (basalt and minerals lining fissures in basalt), and colloids (generated from barrier materials hydrothermal alteration) will be used in these tests since they must be representative of the engineered barrier system. Table 5-8 summarizes the test techniques, equipment, variables investigated, data produced, and analytical techniques required.

5.1.2.2.3.2 Solubility Testing. A summary of the radionuclide solubility data needs and the application of these data to design and performance assessment are summarized in Table 5-9. As noted above, radionuclide operational solubilities (steady-state concentrations) are the principal data needs. Experimental studies for each radionuclide must be indexed to important environmental variables such as temperature, Eh, pH, and solution chemistry. A summary of the test equipment and techniques required to generate these data under specified conditions is shown in Table 5-10.

5.1.2.2.4 Summary of Testing to Date.

5.1.2.2.4.1 Sorption and Colloid Testing. Most of the work completed thus far on radionuclide sorption testing of materials present in the repository horizon has been focused on crushed basalt as the sorbant in order to assess its usefulness as a component of the waste package packing material. Sorption on secondary minerals found in basalt formations has also received some attention (Barney, 1981; Salter et al., 1981b), although available data are restricted to a single sample of secondary minerals. This sample was obtained from a shallow basalt flow (Pomona flow) which is distant from candidate repository horizons. Radionuclide sorption on bentonite clay, a candidate waste package packing materials component, has been studied at 60° and 150°C. Studies are presently underway on radionuclide sorption on hydrothermally altered packing materials

TABLE 5-7. Summary of Data to be Obtained from Radionuclide Sorption Testing.

Data category	Data produced	Measured or controlled parameters	Application to waste package design/performance assessment
1. Radionuclide sorption-desorption on engineered barriers and geologic solids	A. Radionuclide sorption-desorption coefficients and isotherms	Solid composition, groundwater composition, pH, Eh, temperature, time, water:solid ratio, radionuclide concentration, and radionuclide identity	Radionuclide sorption and desorption coefficients or isotherms are essential inputs to radionuclide transport models which predict release rates from the various components of barriers.
	B. Elution curves for radionuclides to develop transport models	Solid composition, groundwater composition, pH, Eh, temperature, flow rate, porosity, column dimensions, radionuclide concentration, and radionuclide identity	Elution curves from sorption flowthrough experiments complement isotherm data to give more accurate estimates of transport. Multiple species of radionuclides can be identified.
	C. Groundwater and solids composition	Starting compositions of solids and groundwater, temperature, time, water:solid ratio, and particle size	Changes in groundwater and solids composition during sorption experiments must be known since these variables affect sorption.
2. Radionuclide sorption/desorption on colloids	A. Radionuclide distribution among colloids-groundwater-solids	Compositions of colloid, solid, and groundwater, pH, Eh, temperature, time, colloid concentration and size, water:solid ratio, radionuclide concentration, and radionuclide identity	The distribution of radionuclides among colloids, groundwaters, and solids must be known to determine the potential for radionuclide transport on colloids.
	B. Elution curves for colloidal particles and radionuclides to develop transport models	Compositions of colloid, solid, and groundwater, pH, Eh, temperature, flow rate, porosity, column dimensions, colloid concentration and size, radionuclide concentration, and radionuclide identity	Elution curves for colloids are needed to determine the potential for colloid migration through various barrier materials.

TABLE 5-8. Summary of Test Techniques Required for Radionuclide Sorption Testing.

Test technique	Test equipment	Parameters investigated	Data produced	Analytical techniques
Batch equilibrium sorption-desorption tests	Teflon or glass reaction vessels at temperatures <100°C. Autoclaves at higher temperatures.	Temperature = 60 to 150°C Eh = +0.6 V to -0.4 V Time = 0 to 60 days Rock:waste = 1:5 to 1:20 Colloid concentration	Radionuclide concentration in groundwater and solids	γ-emitters:GeLi counter β-emitters:βcounter, liquid scintillator α-emitters:αcounter, liquid scintillator
			Groundwater composition	Cations: ICP, AA Anions: Ion chromatograph Carbonate: Total carbon analyzer
			pH	Glass electrode
			Solids characterization	SEM, STEM, X-ray diffraction
			Colloid concentration	Particle counter
Flowthrough sorption-desorption tests	Columns packed with sorbant solids, low-flow-rate HPLC pump, automatic fraction collectors.	Temperature = 60 to 150°C Eh = +0.6 V to -0.4 V Time = 0 to 200 days Flow rate = 0.01 to 1.0 mL/min Column dimensions Diameter = 0.9 - 3.0 cm Length = 2.0 - 20 cm	Same as above plus elution curves	Same as above

Note: AA = Atomic adsorption
HPLC = High pressure liquid chromatographic
ICP = Induction coupled plasma
SEM = Scanning electron microscope
STEM = Scanning transmission electron microscope

TABLE 5-9. Summary of Data to be Obtained From Radionuclide Solubility Testing.

Data category	Data produced	Measured or controlled parameters	Application to waste package design/performance assessment
Key radionuclide solubilities in:			
1. Candidate packing material	Solubility estimates from both oversaturation and undersaturation; characterization of the precipitated solids; speciation of the radionuclides in solution	Temperature, Eh, pH, groundwater chemistry, radiation environment, secondary minerals on altered materials	Provides the source term for performance assessment modeling; may affect container design (to ensure low release limits) or require the addition of buffering materials to the packing material
2. Crushed basalt	Solubility estimates from both oversaturation and undersaturation; characterization of the precipitated solids; speciation of the radionuclides in solution	Temperature, Eh, pH, groundwater chemistry, radiation environment, secondary minerals on altered materials	Provides the source term for performance assessment modeling; may affect container design (to ensure low release limits) or require the addition of buffering materials to the packing material

TABLE 5-10. Summary of Test Techniques Required for Solubility Testing.

Test technique	Test equipment	Data produced	Range of parameters	Required analytical techniques
Solubilities of key radionuclides from oversaturation and undersaturation in crushed basalt and candidate packing material	Autoclaves, sample environmental chambers, source of radiation	Solubility limits under appropriate environmental conditions; characterization of precipitates; speciation of radionuclides in solution	Temperature: 90 to 150°C Pressure: up to 30 MPa Eh, pH: basalt buffered Groundwater: GR-4 composition Radiation field: to be determined	Nuclear counting techniques: α, β, γ Standard analytical techniques for solutions and solids including solution filtration procedures with 15A filters: X-ray diffraction, SEM, STEM, electron probe, ICP, IC

Note: IC = Ion chromatography
ICP = Induction coupled plasma
SEM = Scanning electron microscope
STEM = Scanning transmission electron miscroscope

(75% crushed basalt-25% bentonite) and on bentonite and silica colloids. Site-specific studies of radionuclide sorption on corroded container material have not yet begun. A brief summary of the sorption testing completed to date is given in the following paragraphs.

Measurement of Sorption and Desorption Isotherms. The Freundlich isotherm has been used extensively to describe radionuclide sorption on several types of materials found in the repository horizon (Barney, 1981; Salter et al., 1981a). This empirical equation accurately describes the batch sorption data over a wide range of radionuclide concentrations and for many different combinations of sorption parameters (groundwater composition, Eh, temperature, etc.). It should be stressed that these isotherms do not necessarily represent strict equilibrium distributions but only steady-state values obtained after weeks or months of equilibration. Measurements of sorption and desorption kinetics have been completed for a large number of sorption reactions to determine the equilibration time required to reach steady-state distributions. A summary of the available sorption isotherm data for materials and conditions that might be expected in the repository horizon are shown in Table 5-11. Not all combinations of parameters shown have been used for experiments with crushed basalt and secondary minerals. However, a large amount of sorption isotherm data has been obtained for these materials which can be used in radionuclide transport modeling.

Desorption isotherms and desorption kinetics have been measured for desorption of cesium, strontium, uranium, neptunium, plutonium, and radium from crushed basalt and basalt wafers. It was found that most sorption reactions are irreversible to some degree (i.e., sorption and desorption isotherms for a radionuclide in a given system are different) and that desorption reactions are generally much slower than sorption reactions (Barney et al., 1983). Sorption hysteresis was observed for simple cations such as Cs^{+}, Sr^{2+}, and Ra^{2+} as well as for the actinides. This sorption hysteresis is important because it can greatly affect radionuclide transport. Peak concentrations of radionuclides in groundwater arriving at the accessible environment will be reduced if sorption hysteresis is significant.

The irreversible nature of radionuclide sorption reactions studied thus far gives evidence for chemisorption mechanisms for the radionuclides since most chemisorption reactions are irreversible. This is the predominant sorption mechanism for actinide sorption. However, at least part of the cesium, strontium, and radium is sorbed by ion-exchange mechanisms since major groundwater cations such as Na^{+}, K^{+}, and Ca^{2+} can exchange with these radionuclides.

Sorption of ^{239}Pu, ^{237}Np, ^{238}U, and ^{99}Tc is strongly dependent on the oxidation state of their dissolved species and, therefore, on the Eh of the system. The reduced species is more strongly sorbed in each case. These elements can also form complexes with the anions present in groundwater that change the sorption characteristics of the element. For example, evidence of carbonate complexing of ^{237}Np and ^{238}U in Grande Ronde Basalt groundwater has been obtained (Barney, 1981). The presence of carbonate in groundwater decreases the sorption of these two elements.

TABLE 5-11. Summary of Sorption Isotherm Data Obtained to Date.

Sorbant materials	Groundwater*	Radionuclides	Redox conditions	Temperature (°C)	Time (days)
Crushed basalt: Umtanum Cohassett	GR-1 GR-2 GR-3	Sr, Cs, Se, I Tc, Ra, U, Pu Np, Am	Oxidizing Reducing (with hydrazine)	23 60 150 300	1 - 90
Secondary minerals: Pomona	GR-1 GR-2	Sr, Cs, Se, I Tc, Ra, U, Pu Np, Am	Oxidizing Reducing (with hydrazine)	23 60	1 - 50
Hydrothermally altered backfill: 75% crushed basalt-25% bentonite (reacted at 300°C with GR-3 for 30 days)	"steady-state" groundwater	Tc, Se, Np U, Ra	Oxidizing Reducing (with hydrazine and O_2 removed)	90	7 - 56
450°C-treated bentonite	GR-3	Cs, Sr	Oxidizing Reducing (with hydrazine)	65	

*Groundwater compositions used to obtain sorption data are given in Chapter 6 of the Site Characterization Plan.

Radionuclides that exist as anions in basalt groundwater are weakly sorbed by the solids studied thus far. Sorption of iodine, which probably exists in groundwater as I^- or IO_3^-, is so insignificant that it is difficult to measure. Technetium in oxic groundwater exists as TcO_4^-, which is also weakly sorbed. Dissolved selenium species are either SeO_3^{2-} or HSe^-, depending on the Eh of the system. Both of these anions are weakly sorbed compared to most cations, but their sorption is easily measurable.

The effects of temperature on a number of sorption reactions have been investigated (Ames and McGarrah, 1981). Results of this work indicate that, in general, cesium sorption decreases with increasing temperature, strontium and radium sorption are only slightly affected by temperature in the range of 23° to 85°C, and uranium and selenium sorption increase with increasing temperature.

<u>Flowthrough (Column) Sorption Measurements</u>. Flowthrough sorption measurements that complement the above batch tests are presently underway. They were initiated in FY 1983. Since these experiments are much more time-consuming and difficult than batch studies, fewer data are available. Breakthrough curves for radionuclide sorption on columns of crushed basalt from Umtanum and Cohassett flows at 60°C have been obtained. The GR-3 groundwater (Table 5-12) composition was used for all of these column studies. Radium and uranium sorption was studied using oxidizing conditions (air-saturated) and technetium and selenium using reducing conditions (0.1 <u>M</u> hydrazine). The breakthrough curves (C/C_0 versus pore volumes, where C_0 and C are radionuclide concentrations in the influent and effluent, respectively) appear to gradually level off at C/C_0 values of about 0.15, 0.30 to 0.60, 0.25, and 0.25 for ^{226}Ra, ^{238}U, ^{99}Tc, and ^{79}Se, respectively. A typical breakthrough curve for radium sorption on Umtanum flow basalt is given in Figure 5-7. These levels persist even after many pore volumes of solution have passed through the columns (>5,000 pore volumes in the radium experiments). There are several possible explanations for this type of breakthrough curve, where a constant fraction of the original tracer concentration in the influent is removed by the sorbant in the column. First, it is possible that at least two different species of radionuclide are present in the influent, one weakly sorbed and one strongly sorbed. This is not likely, however, for radium, since it shows little tendency to form complex species and should exist as the hydrated Ra^{2+} ion under experimental conditions used in these column experiments. A more likely explanation is that the sorption reactions are slow and, therefore, nonequilibrium conditions exist in the laboratory columns. Modeling of radionuclide breakthrough and elution curves using solute transport equations will help determine the important mechanisms that control radionuclide transport in the columns.

TABLE 5-12. Compositions of Synthetic Groundwaters Used for Engineered Barriers Experimental Studies.

Constituent	GR-3[a]	GR-4[b]
Na	358	334
K	3.43	13.8
Ca	2.78	2.20
Mg	0.032	--
F	33.4	19.9
Cl	312	405
SO_4	173	4.0
Inorganic carbon	10.8	18.1
Si	35.6	45.0
pH	9.77	9.70

[a]Jones (1982)

[b]Synthetic groundwater composition based on the analysis of a Cohassett flow bottom sample from borehole RRL-2 in the reference repository location.

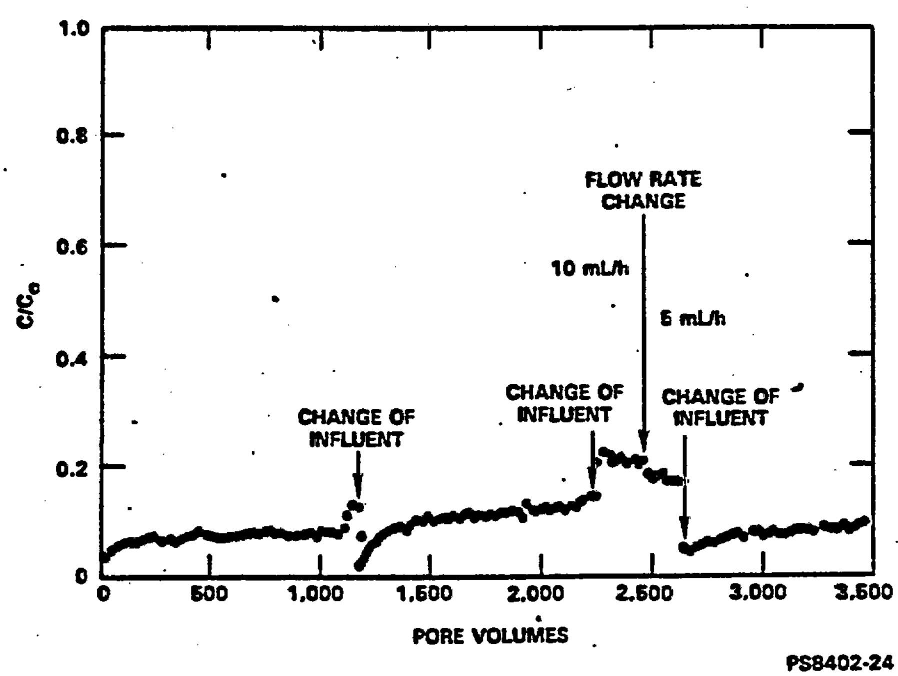


FIGURE 5-7. Breakthrough Curves for Radium Sorption on Umtanum Basalt.

Radionuclide Sorption and Transport on Colloids. Both batch radionuclide distribution tests and flowthrough column tests are underway at the PNL to determine the significance of radionuclide transport on colloidal particles in groundwater. A bentonite colloid, representing a colloid that may be generated from a waste package packing materials or backfill, and two silica colloids, representing colloids produced by glass waste form degradation, have been investigated. In the batch sorption studies, the distribution of uranium, neptunium, technetium, and selenium among colloid, groundwater, and crushed basalt was measured at 60°C under oxidizing and reducing conditions. Radionuclide sorption on the bentonite colloid was most significant for ^{237}Np and ^{99}Tc under reducing conditions and for ^{238}U under oxidizing conditions. Uranium-238 and ^{237}Np sorption on silica colloids was extensive under both oxidizing and reducing conditions, with only small amounts of both going to the basalt. Sorption of selenium and technetium on silica colloids was significant only under reducing conditions. Radium was readily transferred from the colloid to Umtanum flow basalt in the batch experiments.

Transfer of uranium and radium sorbed on silica colloids to crushed Umtanum flow basalt (16 to 60 mesh) was studied in flowthrough experiments at 60°C under oxidizing conditions. Sorbed uranium on colloids and the colloids themselves (200 A mean particle size) readily passed through this column with little transfer of uranium to the basalt. The colloids appeared in the effluent after one pore volume had passed through the column. Significant amounts of radium were transferred to the basalt in similar experiments, however. These results are in general agreement with the results from the batch tests.

5.1.2.2.4.2 Solubility Testing. Previous studies that are relevant to solubility determinations for key radionuclides fall into several broad categories:

- Sorption studies in which precipitation of a radionuclide is inferred (e.g., Barney, 1981 and 1982)
- Studies in which soluble radionuclides were dissolved in aqueous solutions and reprecipitated as more stable solids (e.g., Barney, 1981)
- Studies aimed at determining the solubility of key radionuclides in the presence of basalt from oversaturation (unpublished results from work performed at the PNL for the BWIP).

The first two study types did not have solubility determinations as a goal and, consequently, precipitation was not always demonstrated. Precipitates, if observed, were not characterized for comparison to theoretical predictions of solubility. In addition, these experiments were performed with a variety of solution compositions, some of which are not closely similar to groundwater compositions in the reference repository location of the Hanford Site. Some of these experiments were conducted in the absence of basalt, and therefore the potential effects of this component (with respect to reaction kinetics or attainment of equilibrium) cannot be judged at this time.

The third study represents the only set of experiments specifically designed to yield estimates of solubilities under relevant environmental conditions for a nuclear waste repository in basalt and was initiated in FY 1983 by the PNL under contract to the BWIP. These are sorption-isotherm solubility studies carried out at 60°C in the presence of basalt. An important component of these studies is the characterization of the basalt surfaces and filtered particulates in order to identify the solid phase(s) responsible for controlling radionuclide solubility. While this overall approach to solubility is a promising initial step, several problems exist. One difficulty encountered in all previous experimental studies focuses on the question of Eh control in solution. It is believed that the Eh of the basalt geochemical system is very reducing (-0.45 $\pm$ 0.07 V; DOE-RL, 1982). Attempts to reproduce this low Eh in previous experiments has been by use of hydrazine (N_2H_4) in which an irreversible reaction produces electrons as follows:

$$N_2H_4 + 4\,OH^- = N_2 + 4H_2O + 4e^- \qquad (7)$$

The resultant solution is not redox buffered but is very reducing. Furthermore, it is possible that the radionuclides and/or mineral surfaces may interact with hydrazine, thereby complicating the interpretation of the results. In addition, hydrazine can react in basic solutions to produce hydrazinium ions ($N_2H_5^+$) that may compete with radionuclides for cation exchange sites on colloids and basalt. These are potentially serious shortcomings that need to be addressed in the future solubility studies.

A further limitation of all previous solubility studies is the low temperatures at which they were conducted. At present, results are available only for temperatures of 60°C. As noted above, thermal analysis of the waste package environment yields temperature estimates of approximately 100° to 150°C for the packing materials and disturbed rock zone (depending upon the waste form) at the beginning of the post-containment period while temperatures in this region are still well above the ambient temperatures of approximately 50 to 60°C (DOE-RL, 1982).

Finally, no consideration of the potential effect of a radiation field on radionuclide solubilities has been incorporated into experimental studies conducted to date. The possibility of modification of radionuclide behavior due to radiation-induced changes in geochemical environment is to be addressed in future testing.

5.1.2.2.5 <u>Planned Testing</u>.

5.1.2.2.5.1 <u>Sorption and Colloid Testing</u>. Testing plans for radionuclide sorption can be divided into several categories:

- Measurement of sorption and desorption isotherms for additional solids materials and groundwater compositions using the batch method and measurement of sorption capacity for these materials

- Flowthrough measurements of radionuclide elution and breakthrough curves and modeling of radionuclide transport in laboratory columns

- Development of methods for controlling and measuring Eh in laboratory sorption experiments

- Laboratory measurement of colloid transport through engineered and geologic barriers in the repository horizon and radionuclide distribution among colloids, groundwaters, and immobile solids in groundwater pathways.

Measurement of Sorption and Desorption Isotherms. Sorption and desorption isotherm measurements of key radionuclide sorption on solid materials expected in the groundwater flow path within the repository horizon will be continued. Additional materials to be studied include hydrothermally altered materials (basalt packing materials and backfill), corrosion products of container degradation, and a new groundwater formulation representative of the candidate repository horizon. Additional materials may be added as more information becomes available on the waste package design and the alteration of engineered and geological materials. For materials on which radionuclides are irreversibly sorbed, their sorption capacity will be determined.

The effects of groundwater composition also will be determined. This work will identify important groundwater variables and yield information on radionuclide species and sorption-desorption mechanisms. Other variables to be studied include Eh, temperature, solid/solution ratio, and time.

Flowthrough Sorption Measurements. Column studies will continue to be emphasized in future sorption work. Radionuclide breakthrough and elution curves for columns filled with hydrothermally altered materials (crushed basalt, packing materials, and backfill materials) will continue to be measured. The types of experiments to be performed include both constant tracer feed to the column (which yields breakthrough curves) and pulse input (which yields elution curves). These curves will be interpreted in terms of radionuclide sorption and desorption mechanisms that affect transport through the laboratory columns (e.g., nonlinear sorption, sorption hysteresis, kinetics, etc.). Appropriate transport equations will be applied to the data to model these processes and extrapolate the laboratory data to site and waste package conditions. A radionuclide sorption/transport in situ confirmatory test is planned by the BWIP Site Department.

In addition to the porous flow column studies, flowthrough sorption measurements using natural basalt fractures in laboratory columns will be completed. Fracture flow will be the predominant flow type in dense basalt. Drilling cores containing natural fractures will be identified, characterized, and machined to fit laboratory flowthrough columns. Sorption studies on flow top and interbed materials is the responsibility of the BWIP Site Department.

Methods for Eh Control. Practical methods for controlling Eh in sorption experiments will be investigated as alternatives to the presently used method of adding hydrazine to yield reducing conditions. When reducing sorbants, such as basalt, are used in sorption experiments, it may be possible to remove oxygen from the system and allow the solid to control Eh. This will require performing the experiments in a sealed apparatus (probably made of glass) that does not allow diffusion of O_2 through the walls. Inert atmosphere gloveboxes will not reduce the O_2 level to a low enough value to be useful for sorption measurements of some radionuclides (e.g., Tc) in basalt/groundwater systems. Very small amounts of O_2 are likely to greatly increase the effective Eh of these solutions since they are expected to be poorly poised. Several methods for Eh measurement will be studied: electrode measurement, redox indicator dyes, and measurement of redox couples.

Radionuclide Sorption and Transport on Colloids. The potential for colloid transport through engineered and geologic barriers in the repository horizon will be evaluated. Laboratory columns containing crushed, altered basalt, altered waste package packing materials, and repository backfill material will be used to measure convective transport of radioactively labeled colloids through these materials. Experimental parameters that are expected to control colloid transport, such as ionic strength of the groundwater (controls flocculation of colloid suspensions), groundwater flow rate, colloid size distribution and composition, and porosity of the column bed material, will be evaluated over ranges of values expected in the repository horizon.

An important component of these studies is to determine the importance of mechanical filtration of colloidal particles in fractured basalt. Apps et al. (1983) have evaluated the interaction of diffusive transport and gravitational settling of colloids theoretically and have concluded that migration of even 10 Å particles will be prevented by the substrate in porous or fractured media where the pore sizes or fracture apertures are ≤ 1 mm. Recent modeling studies (unpublished results and Section 5.1.2.3.4 of this document) strongly suggest that solute transport in the packing materials and dense basalt is diffusion controlled; therefore, the analysis of Apps et al. (1983) may be meaningful. For example, Long et al. (1983) have found that filled fracture widths for the Cohassett flow and Umtanum flow basalts are <1 mm. Estimates by visual examination of apertures for open fractures in the dense interior of these basalt flows are considerably <1 mm. Consequently, mechanical filtration of even small colloidal particulates is anticipated in the dense interior of the basalt if their migration is diffusion controlled.

Measurement of the distribution of key radionuclides among groundwaters, colloids, and immobile solid materials will be continued in parallel with the above work. Both batch equilibration and flowthrough methods will be used to measure this distribution. Experimental parameters to be evaluated during these studies include colloid composition and concentration, groundwater composition and Eh, type of immobile solid (altered packing materials and backfill material or altered basalt), and temperature.

The preparation and characterization of colloids used in these experiments are critical steps in completing the work outlined above. Colloids that are representative of those generated by degradation of the waste package must be used. The waste form, container, packing materials, and backfill can potentially generate particles of different compositions (silica; oxides of iron, chromium, and nickel; bentonite colloids; etc.). Characterization of these colloids must include measurements of particle size distribution, composition, zero point of charge, and agglomeration of colloidal particles.

5.1.2.2.5.2 <u>Solubility Testing</u>. Solubility studies are being designed to incorporate potential contributions from a variety of experimentally adjustable parameters including:

- Groundwater composition (including pH)
- Temperature
- Eh
- Radiation field
- Solid substrate.

As presently configured, these experiments will be conducted at 90° and 150°C using a synthetic groundwater formulation based upon reference repository location groundwater chemistry in the Grande Ronde Basalt formation (see Table 5-11, Section 5.1.2.2.4.1). As noted above, the temperatures have been chosen to bracket the range of temperatures calculated to be encountered by the respective materials when radionuclides are released from the waste package.

Of critical importance in these experiments will be the maintenance of the Eh at a value consistent with present knowledge of redox conditions in the basalt geochemical system by a method(s) that does not interfere with the experiment. Hydrazine has been used in past experiments to simulate reducing conditions because it rapidly reduces most key radionuclides dissolved in groundwaters, it produces innocuous reaction products (N_2 and H_2O), and it does not complex radionuclides at the pH present in basalt groundwaters. As noted in Section 5.1.2.3.4.2, the use of hydrazine as a reducing agent has been frequently challenged because it is an irreversible couple, does not buffer the Eh, and may interfere with radionuclide behavior.

A task that will be addressed early in FY 1984 is an evaluation of alternative methods of controlling solution Eh without the use of hydrazine. Based upon the results of unpublished studies, the BWIP and the Savannah River Laboratory have had some success with basalt/water systems that are deoxygenated by application of a vacuum or by passing purified argon gas through the samples. It appears that dissolved oxygen levels of approximately 10^{-6} <u>M</u> are achieved. While this concentration of dissolved oxygen still would suggest an Eh of approximately +0.6 V at pH = 9.5, experiments with added TcO_4^- demonstrate rapid reduction to technetium(IV) and sorption and/or precipitation in the presence of basalt. This should occur only at relatively low values of Eh. In other words, dissolved oxygen is not poising the system, and it might be suspected that active surfaces of the basalt are in control of the redox state of the solution.

There are several potential techniques by which deoxygenation may be approached. These include:

- Vacuum degassing (unpublished results of the BWIP)
- Sparging with purified inert gas (argon) (LANL, 1982; Jantzen, 1983)
- Use of a potentiostat (LANL, 1982).

The initial goal is to explore these techniques and settle on the one that is most reliable and easily applied. The second part of this task is to use several complementary but independent techniques to determine (bracket) the apparent or operational Eh of the system. These techniques may include the use of:

- The As^{3+}/As^{5+} redox couple (Lane et al., 1983)
- Redox dyes (LANL, 1982)
- Platinum electrodes (Jantzen, 1983)
- Other redox couples.

The ultimate goal of this task is to calibrate a basalt/water and basalt/bentonite/water system for Eh without introducing any foreign materials.

The matrix of solubility tests includes two solids (basalt and packing materials), two baseline temperature conditions (90° and 150°C) and a series of key radionuclides (selenium, technetium, radium, uranium, neptunium, and plutonium) that have been identified by the BWIP through previous, unpublished modeling efforts. The starting solids will be pre-altered (e.g., 30 days in an autoclave at 300°C and 30 MPa) so that the surfaces of the grains are coated with appropriate secondary phases. These will be static tests using GR-4 groundwater (see Table 5-12) and reference Cohassett flow basalt or basalt/bentonite as starting materials. The 90°C tests will be conducted in glass, quartz, or plastic sample containers in a shaker bath. The tests run at 150°C will use autoclaves at a pressure of 30 MPa.

In order to estimate the solubilities of key radionuclides, the BWIP utilizes thermodynamic calculations such as those described in Early et al. (1982) as a first-order approximation. These estimates are now being refined by an empirical approach that is discussed in this section.

As stated previously, it is possible to approach solubility either from undersaturation or oversaturation conditions. Undersaturation techniques involve adding the solid, which is known or assumed to control solubility for a specific radionuclide, to the appropriate experimental aqueous system and waiting until an equilibrium level of the radionuclide is observed in solution. Problems associated with the choice of appropriate solid and the lengthy time required to reach equilibrium are inherent in this method. Alternatively, in solubility experiments approached from oversaturation, the aqueous solution is spiked with a radionuclide such that supersaturation occurs followed by precipitation. This experimental design more closely approximates anticipated conditions in a repository where radionuclide-bearing solutions will migrate down a thermal gradient away from the waste package and become oversaturated with respect to these components.

The BWIP has chosen initially to adopt the oversaturation technique for experimentally estimating solubility limits for key radionuclides. This technique is not without problems; however, formation of colloids and demonstrating attainment of equilibrium may complicate interpretations. Evidence suggesting formation of colloids in this type of experiment is discussed in Section 5.1.2.2.4.1.

The original experiments of this type, which are applicable to ambient conditions in the site system, were conducted with reference to Grande Ronde Basalt groundwater, GR-3 (see Table 5-12), in the presence of crushed basalt from both the Umtanum and Cohassett flows at 60°C. The solutions were spiked with an increasing amount of a radionuclide until the solubility limit was reached.

Figure 5-8 shows the type of information that can be obtained from these experiments and illustrates how the resulting data can be interpreted. In this figure, the equilibrium concentration of a radionuclide in solution is plotted against the initial spiked concentration. In an experimental basalt/water system where neither sorption nor precipitation of the radionuclide occurs, the experimental data should lie along Line A for which the amount of radionuclide added is equivalent to that observed in solution. If the basalt is capable of sorbing some of the radionuclide, a sorption isotherm (such as the straight section of Line B) results, displaced downward from Line A by an amount proportional to the amount of the radionuclide sorbed. Finally, as the concentration of the added radionuclide exceeds its solubility in the solution, Line B will achieve a plateau such that the final measured concentration in solution does not change with increases in the amount added. The concentration of the radionuclide in solution at the plateau can be interpreted as the solubility limit. Preliminary solubility data have been obtained for uranium and plutonium in the presence of basalt using this technique (Table 5-13). In addition, experimental studies have been initiated for other key radionuclides (selenium, technetium, lead, neptunium, and americium).

Related solubility experiments from undersaturation will accompany those described previously and are crucial for bracketing the effective solubility value. If possible, the solid product from oversaturation studies (basalt or packing materials with adhering radionuclide-bearing phase(s)) will be used as starting material and will be placed in

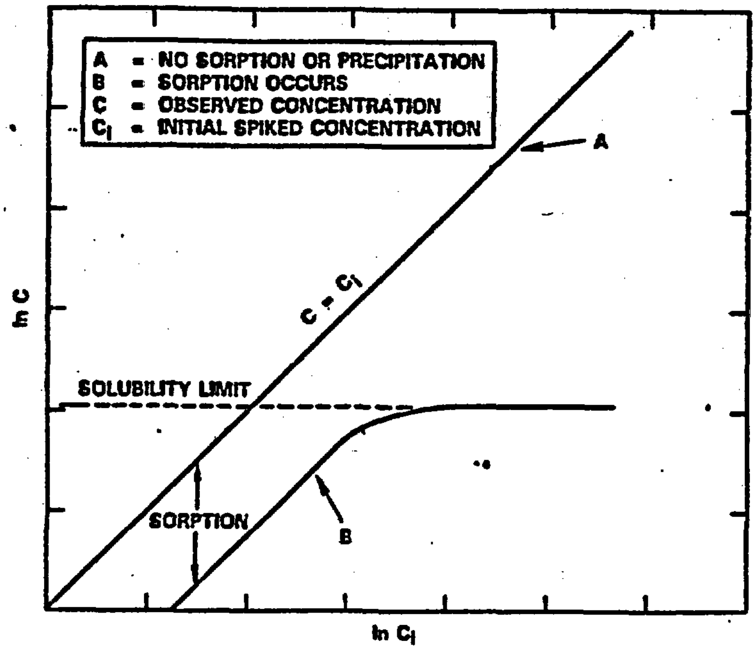


FIGURE 5-8. Hypothetical Plot of ln C Versus ln C_i Obtained for a Radionuclide in a Solubility Experiment.

TABLE 5-13. Preliminary Solubility Estimates for Uranium and Plutonium in Reference Grande Ronde Basalt Groundwater in the Presence of Crushed Basalt[a] at 60°C.

Radionuclide	Redox conditions[b]	Solubility[c] (mol/L)	Precipitate observed[d]
^{233}U	Oxidizing	7×10^{-5}	Schoepite ($UO_3 2H_2O$)
	Reducing	1×10^{-6}	Uraninite (UO_2)
^{238}Pu	Oxidizing	10^{-10} to 10^{-8}	$PuO_3 \cdot H_2O$
	Reducing	1×10^{-9}	PuO_2

[a]Umtanum flow entablature and flow top and Cohassett flow entablature.

[b]Oxidizing - air saturated; Reducing = 0.1M (H_2H_4).

[c]Solubility estimates are based upon solutions that were passed through 15Å filters prior to analysis.

[d]Identification of precipitates is based upon visual examination only. A detailed characterization is planned.

GR-4 groundwater at 90° or 150°C, respectively. Use of these solids will guarantee that the phase(s) controlling the solubility of each radionuclide is present in both the over- and under-saturation experiments.

These solubility studies will not have a predetermined duration since preliminary work with a number of radionuclides have indicated that the kinetics of nucleation may be on the order of several months or longer. Consequently, the run charges will be sampled at appropriate intervals until precipitation is evidenced from the shape of the C versus C_i line (see Fig. 5-8).

A final, necessary step to the solubility studies is the identification of the precipitated radionuclide phases by microprobe, scanning electron microscope, scanning transmission electron microscope, or X-Ray diffractometer, or some combination. Hopefully, this information, when compared to the theoretical computations using thermodynamic data, will lead to a reasonable coincidence of the results.

The solutions generated in some of the solubility tests will be subjected to additional study to determine the redox speciation of the actinides. Standard techniques, such as those outlined in Cleveland et al. (1983), will be used for this investigation.

All solutions generated in these solubility studies will be sequentially passed through a series of filters (e.g., 1 µm, 0.45 µm, 0.1 µm, 15 Å). There are two reasons for this step: (1) solubility estimates will be based upon the 15 Å filtrate which is assumed to be colloid-free and (2) sequential filtering followed by analysis of the respective filtrate for the radionuclide will yield crude size distribution information for the colloidal materials.

5.1.2.2.5.3 Groundwater Radiolysis Testing. Exploratory tests have shown that gamma radiolysis of reference Grande Ronde Basalt groundwater containing 700 mg/L methane can produce organic polymers similar to polyethylene (Gray, 1983). Interactions of radionuclides with these polymers could potentially affect radionuclide sorption and solubility behavior. The possibility of the formation of organic complexing agents must be investigated, as well as the sorption of radionuclides on the polymeric colloids produced by radiolysis.

The radiolysis tests are designed to evaluate effects of both gamma and alpha radiolysis on the chemical environment of a waste package. Conditions during testing must simulate those of the waste package after the container is breached and radionuclide solubility and sorption are operating mechanisms. The groundwater composition and waste package constituents must be chosen to simulate those present after this containment period. The experimental parameters to be investigated include the following:

- Irradiation temperature (50° to 100°C initially, temperatures up to 250°C will be used but will require development of experimental equipment)
- Radiation dose and dose rate (0 to 10^6 rad/h)

- Initial groundwater composition (GR-4 groundwater with methane concentrations of 0 to 700 p/m)
- Presence of waste package constituents such as bentonite, crushed basalt, and iron (individually and in combination).

After irradiation, the radiolytic products will be characterized. These measurements will include:

- Gas pressure and composition
- Solution Eh and pH
- Solution concentration of H_2O_2, NO_3^-, and other ions
- Mass of polymeric solids produced
- Chelating capacity of solutions
- Sorption capacity of solids
- Molecular weight distribution of solids
- Infrared spectra of solids
- Carbon, hydrogen, nitrogen, and oxygen fractions of the solids.

Some of the above measurements will be complicated by the presence of waste package constituents, particularly bentonite. The problem lies in the separation of the polymeric solid from bentonite. It may be possible to remove the polymers by solvent extraction or flotation but this will require additional development.

Gamma radiolysis testing will be performed in quartz vessels in a ^{60}Co facility. Alpha radiolysis testing will use ^{238}Pu as the alpha source. Since plutonium is only very slightly soluble in Grande Ronde Basalt groundwaters, it will be necessary to keep ^{238}Pu particles in suspension by agitation of experimental mixtures.

Detailed plans for measuring the effects of radiolysis on radionuclide solubility and sorption cannot be developed until the results of the above tests are obtained and evaluated. Also, the dose rate of the groundwater versus time must be known in order to design meaningful tests. Dose rate calculations for proposed waste package designs are being completed at this time.

5.1.2.2.6 Logic Diagram. The data generated in the sorption, colloid, and solubility testing have been planned to follow a logical flow so that appropriate data are available when needed for major milestones associated with waste package and BWIP licensing activities. This flow is shown in the logic diagram for sorption and solubility (Fig. 5-9 and Fig. 5-10).

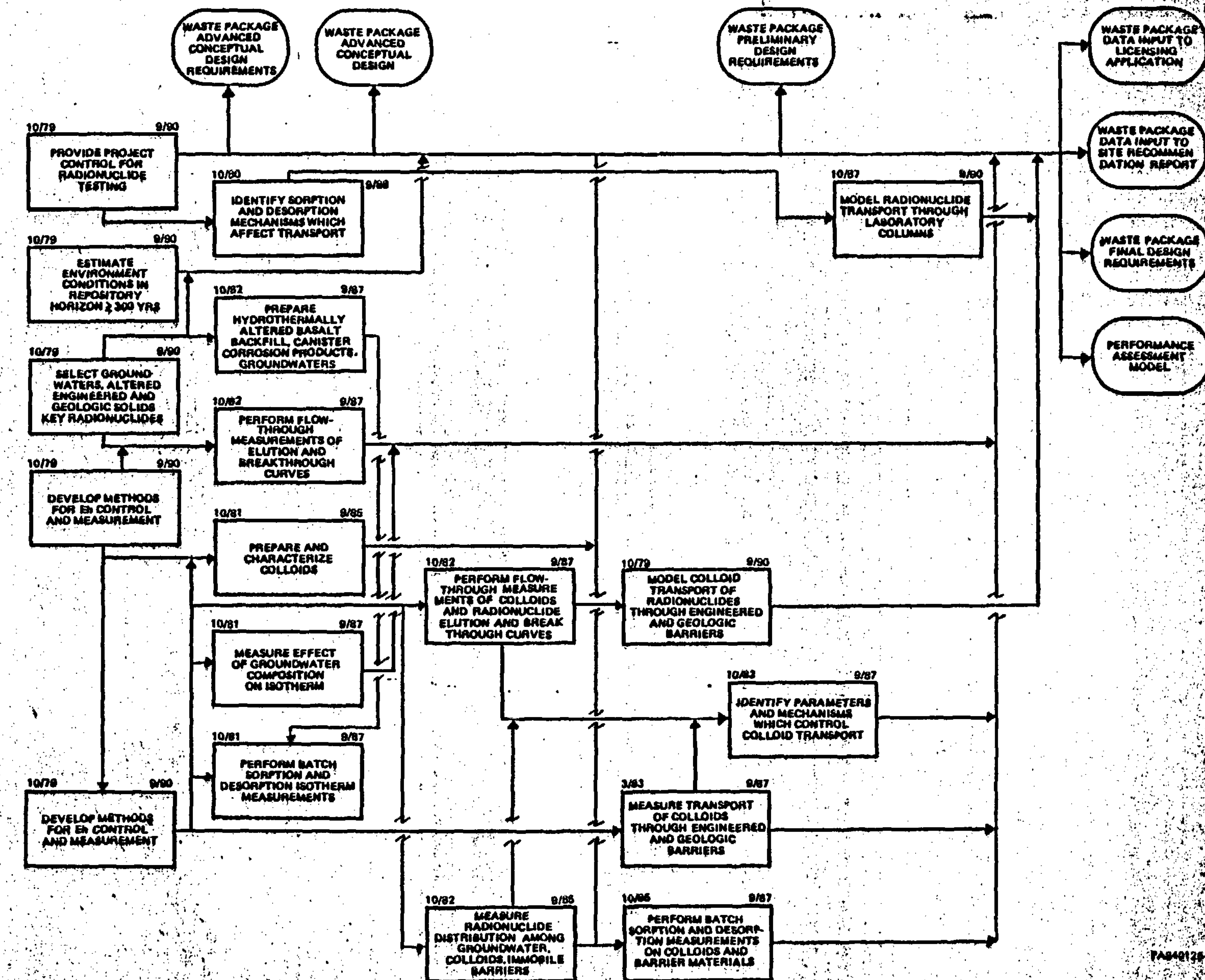


FIGURE 5-9. Radionuclide Sorption Logic Diagram.

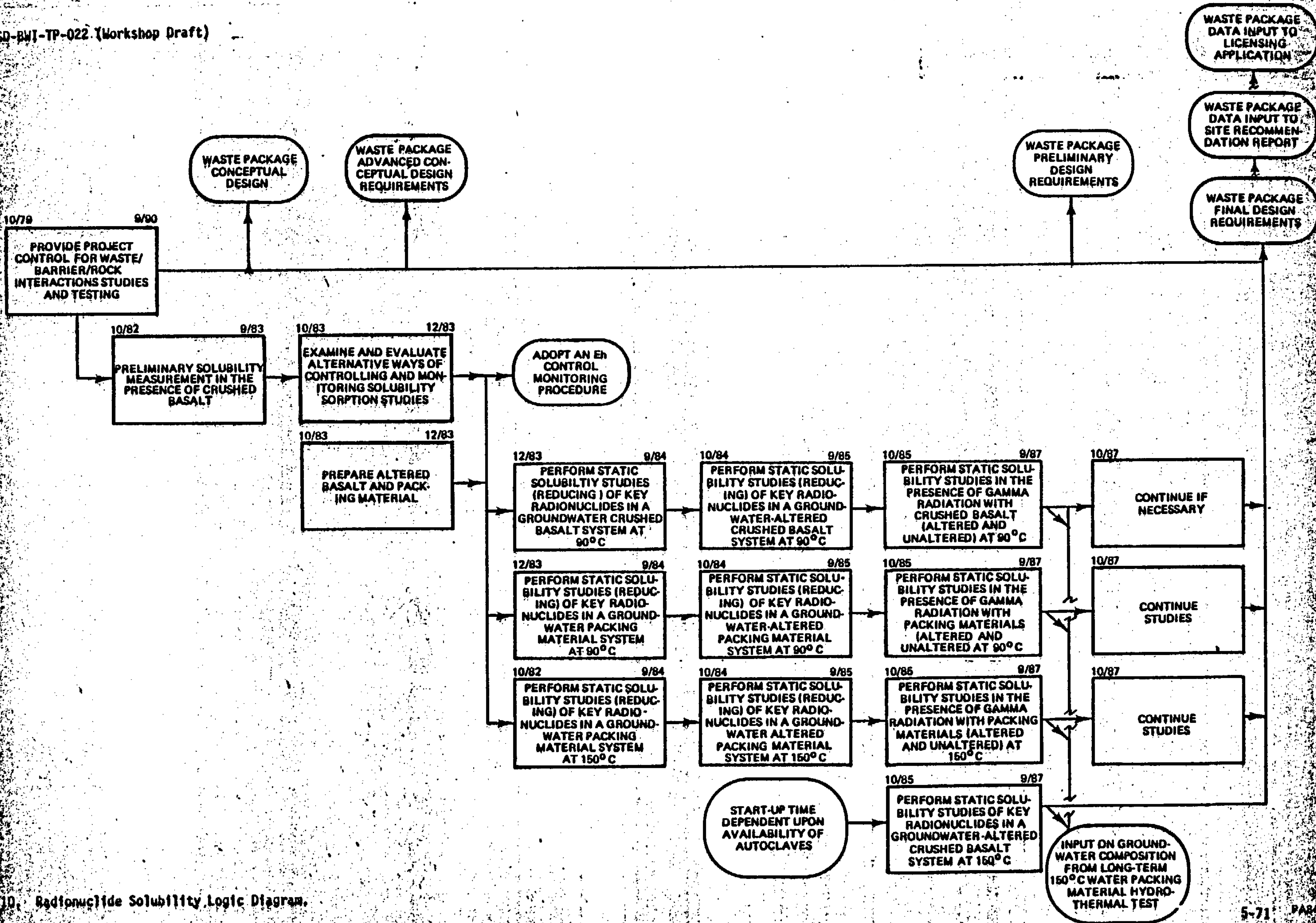


FIGURE 5-10. Radionuclide Solubility Logic Diagram.

5.1.2.3 Container Materials Testing.

5.1.2.3.1 Introduction. The container materials studies for the BWIP have progressed from the literature review stage through the screening of several materials to the selection of a reference material and two backup materials. Based on the results of the literature and early corrosion screening tests, low carbon steel, Fe9Cr1Mo alloy steel, and Cupronickel 90-10 were selected for further testing. Several nickel-base alloys also exhibited excellent corrosion resistance in screening tests but were not selected because of cost considerations. These will receive renewed attention if the three materials selected prove unsatisfactory in subsequent testing. With the selection of the candidate container materials, it is necessary to focus testing efforts on the evaluation of two general categories of materials behavior: (1) environmental effects on mechanical property behavior and (2) environmental effects on material integrity or corrosion behavior. Generation of these data requires testing over a wide range of variables using an approach that will lead to an understanding of the materials behavior in a nuclear waste repository in basalt. A mechanistic understanding of the container materials behavior is essential in order to extrapolate relatively short-term data to time periods over which the waste packages are expected to provide containment. Statistical analysis of the container materials test results will be performed to allow design of containers with the required reliability.

The data needs and specific testing requirements for container materials are described in more detail in the following sections. The use of the data generated by these tests and the timing of data availability are also discussed.

5.1.2.3.2 Objective and Justification. The overall objective of the container materials studies is to provide sufficient data on the behavior of reference and backup container materials exposed to the simulated environment of a nuclear waste repository in basalt to assess their ability to meet container design and performance reliability requirements.

The design of a waste package to contain nuclear waste requires a knowledge of the mechanical, physical, and corrosion behavior of the container material. The physical properties of the container material are primarily a function of temperature and are independent of the aqueous environment; therefore, they can be obtained from the literature and handbooks. However, mechanical properties coupled with corrosion behavior (e.g., stress corrosion cracking) can be very sensitive to the total environment and must be measured under the hydrothermal conditions closely simulating the repository environment. Mechanical property and corrosion test data are essential to the design and performance assessment of the container expected to provide a reasonable assurance of waste containment for a period of 300 to 1,000 yr.

5.1.2.3.3 Summary of Data Needs. A summary of the container material data needs and the application of these data to design and performance assessment are summarized in Table 5-14. The data needs are organized into the three categories: mechanical, physical, and corrosion properties. Since physical properties are primarily a function of material composition and temperature, these are tabulated in the literature or material handbooks and, therefore, no additional testing is required. The effects of the expected repository environment on mechanical properties and corrosion behavior are dependent on many variables including temperature, groundwater chemistry, Eh, pH, etc. as listed in Table 5-15. A summary of the test equipment and techniques required for generating the data is also presented in Table 5-15.

5.1.2.3.4 Summary of Testing to Date. Early screening data were generated using electrochemical measurement techniques on low-carbon steel and Cupronickel 90-10 as well as several other candidate container alloys (nickel- and titanium-base alloys). The data were generated at 90°C using a high-purity argon sparge of the synthetic Grande Ronde Basalt groundwater to reduce the oxygen concentration level below measurable levels. These tests did not include packing materials in contact with the specimens. There is no assurance that the reducing conditions expected to exist in a closed repository were achieved using this technique. The low-carbon steel exhibited a higher corrosion rate than the Cupronickel 90-10 in this test. However, subsequent longer term corrosion tests, conducted in small pressure vessels (made by Parr) for times of up to 1 mo in both oxic and anoxic environments at 150° and 250°C, indicated very little difference in the corrosion behavior of these two alloys. Both materials exhibited acceptable corrosion behavior with rates in the range of 5 to 10 µm/yr (0.2 to 0.4 mil/yr) under anoxic conditions at 250°C.

More recently, refreshed autoclave corrosion tests were conducted by Westerman (1983a and 1983b) on three ferrous alloys. These tests provided general corrosion data for no gamma radiation during an exposure period of up to 17 mo and in the presence of a gamma radiation field (3×10^5 rad/h) for up to 13 mo. The tests were conducted under oxic groundwater conditions (approximately 0.3 mg/L oxygen at autoclave outlet) at a relatively high flow rate (35 mL/h) with no packing materials in contact with the specimens. Corrosion data for low-carbon steel generated by Westerman (1983a and 1983b) under the same conditions revealed similar behavior to the ferrous alloys at exposure times of up to 8 mo. The uniform corrosion rates in the absence of gamma radiation were relatively low at test times of 3 mo and beyond (8 µm/yr (0.3 mil/yr) at 250°C and 13 µm/yr (0.5 mil/yr) at 150°C based on linear kinetics). Testing in the gamma radiation field (Westerman, 1983b) revealed an enhancement of corrosion rate by a factor of approximately two to three over that observed without radiation.

TABLE 5-14. Summary of Data to be Obtained from Container Materials Testing.

Data category	Data produced	Measured or controlled parameters	Application to waste package design and performance assessment
<u>Corrosion behavior</u> • Environmental effects - Aqueous (film formation behavior) - Air/steam environment • Potential corrosion mechanisms - Uniform - Pitting - Crevice - Intergranular - Bacterial Laboratory testing is required to characterize the corrosion behavior of container materials as a function of time under conditions anticipated in the waste repository environment.	• Corrosion rate • Degradation mode	Key variables include temperature, Eh, pH, radiation, groundwater chemistry, flow rate, and material condition.	(1) Corrosion allowances (container wall thickness will be established in container design on the basis of measurable corrosion behavior and required container lifetime. (2) Corrosion data and mechanisms will be used with strength and ductility data to predict failure times and failure modes in performance analysis.

TABLE 5-15. Summary of Test Techniques Required for Container Materials Testing.

Test technique	Test equipment	Data produced	Range of parameters	Required analytical equipment
1. Slow-strain-rate	-Tensile test frame -Strain measurement device -Load cell -Autoclave -Solution reservoir -Reduced gage section tensile specimens	-Strength (lb/in^2) proportional elastic limit, ultimate tensile strength -Ductility (%), elongation, reduction of area -Fractography fracture mode	-Temperature (50° to 300°C) -Strain rate (1×10^{4} to 2×10^{-7}/s) -Radiation (γ) up to 2×10^{6} rad/h) -Material condition • Wrought • Cast • Weldment	-Temperature and pressure measuring instrumentation -Load and strain readout -Groundwater solution analysis -Scanning electron microscopy analysis of fractures
2. Crack growth	-Servo-hydraulic test frame -Load cell -Autoclave -Solution reservoir -Compact tension and wedge-opening loading fracture mechanics specimens	-Time to onset of cracking (static) for given stress intensity factor -Crack growth rate (cyclic) for stress intensity factors	-Temperature (50° to 300°C) -Stress ratio (0.05 to 1.0) -Radiation (γ) (up to 2×10^{6} rad/h) -Material condition • Wrought • Cast • Weldment	-Temperature and pressure instrumentation -Load readout -Groundwater solution analysis -Secant method for analyzing crack growth from compliance measurements
3. Corrosion behavior	-Pressure vessels -Refreshed autoclaves -γ-field radiation -Groundwater solution reservoir -Atmospheric air/steam chambers -Thin, rectangular corrosion specimens	-Corrosion rate -Pit growth rate -Degradation mode	-Temperature (50° to 300°C) -pH (6 to 10) -Flow rate (static to low) -Groundwater chemistry variations in Cl^-, F^-, SO_4, CO_3, etc. -Packing mixture (0 to 100% bentonite) -Material condition: wrought, cast, carbon content, weldments, and surface condition -Radiation (γ) (up to 2×10^{6} rad/h)	-Temperature and pressure instrumentation -Groundwater solution analysis -Corrosion product identification and particle size analysis -Statistical treatment of the data to provide confidence limits (standard deviation) -Electrochemical corrosion testing device

9.3 DATA ACCEPTANCE

The overall objectives of the BWIP barrier materials testing program are to provide necessary data and analyses for (1) developing waste package designs and (2) quantitatively evaluating component and waste package behavior (reliability analyses) relative to the numerical performance objectives defined by the NRC (1983a). The data acceptance requirements are shown in Table 9-1.

9.3.1 Are Test Data Acceptable

Numbered laboratory notebooks shall be used to document the acquisition of all test data, including material specimens and objective evidence. To be acceptable, test data must satisfy the requirements set forth in Table 9-1.

Acceptable test data are released and archived as described in Section 5.4.1. Discrepant test data are reported, dispositioned, and archived in accordance with the change control requirements presented in Section 9.4.

9.3.2 Are Additional Barrier Materials Test Data Needed

The barrier materials test data required to support the development of waste packages for a nuclear waste repository in basalt are established in this test plan. Changes to test requirements shall be controlled and shall be documented in revisions to this test plan, procedures, or instructions.

The decision regarding the need for additional barrier materials test data will be based on reliability analysis and on requirements set forth in this test plan. The acquisition of additional data beyond that specified in this plan will be approved through the use of the change control process.

9.4 DISCREPANCY REPORTING AND CHANGE CONTROL

As a result of the acceptance determination described above, certain test data and predictive models based on the test data may be found to be unacceptable. The reporting of discrepant conditions and the control of changes to requirements shall be in accordance with the requirements of this section.

TABLE 9-1. Data Acceptance Requirements.

Are test data acceptable?	Are additional data needed?
Peer review by management, performance assessment, modelers, waste package, designers, and scientists • Acceptable precision • Acceptable accuracy • Controlled experiments • Statistically designed experiments • Reproducible results • Calibrated test equipment • Acceptable format for input to design and performance assessment • Quality assurance (trained personnel, approved procedures, correct records) • Acceptable documentation, traceability, and archiving • Data meets reliability specifications	• Data meets tests objectives for design and performance assessment requirements • Data meets reliability specifications

9.4.1 Discrepancy Reporting

Any deficiency in characteristics, documentation, or procedure that renders the quality of items, activities, or data unacceptable or indeterminate shall be documented on a nonconformance report and dispositioned in accordance with approved procedures. Appropriate corrective action shall be implemented to resolve conditions that are found to have an adverse effect on quality.

9.4.2 Change Control

The BWIP exercises a formal management control system to assure proposed changes are properly approved and subsequently implemented and completed. This system is comprised of a variety of elements that collectively manage proposed changes to baselined documents, control schedules, and identify authorized budgets. A structured classification system assures each proposed change receives the appropriate level (i.e., DOE/Rockwell) of approval. Changes resulting from disposition of nonconforming conditions are also processed through the system.

10.0 ORGANIZATION AND FUNCTIONAL RESPONSIBILITIES

The Engineered Barriers Department is responsible for planning and implementing materials testing and analytical activities to support the development of waste package design and performance assessment. The organization chart for the Engineered Barriers Department is shown in Figure 10-1. The chart also shows the organization of the Joint Hot Cell Testing Program.

Within the Engineered Barriers Department, the BWIP Materials Testing Group is responsible for hydrothermal testing candidate materials in the 2101-M Laboratory and areas of the 222S Laboratory. The Engineered Barriers Design Development and Analysis Group is responsible for conducting engineering studies and analyses to support the preparation of design requirements for the design of waste packages. The Near-Field Geochemistry Group within the Engineered Barriers Department is responsible for the successful completion of the BWIP materials testing program, which includes the Joint Hot Cell Testing Program. The Joint Hot Cell Testing Program, consisting of personnel from the Engineered Barriers Department, WHC, and PNL, will be conducting hydrothermal testing of waste package materials in the presence of doped- and fully radioactive waste forms. Analytical and hot cell test facilities to be used are located in the 300 Area. The Joint Hot Cell Testing Program is directed by the BWIP with a BWIP Project Manager (not shown in Fig. 10-1) responsible for the activities of each testing, analytical, and data evaluation team.

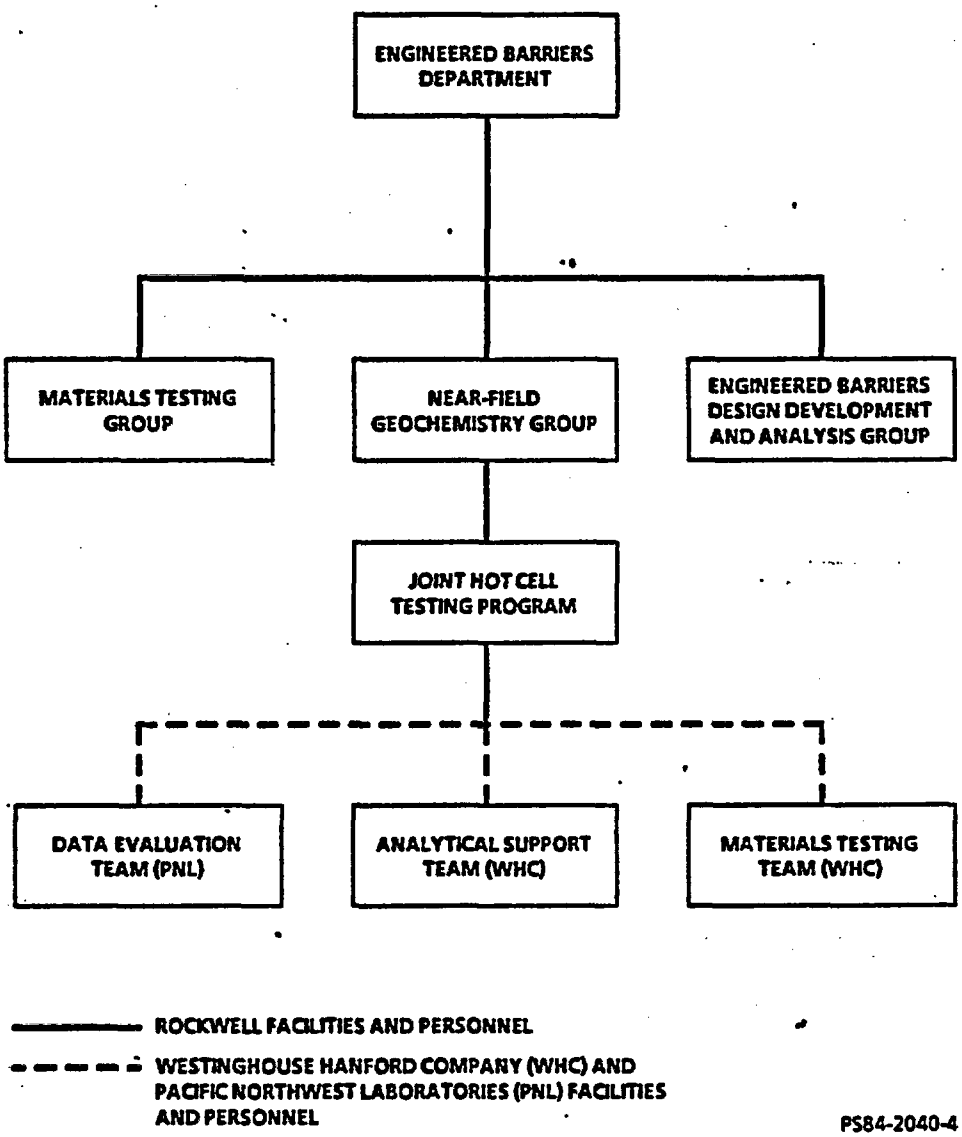


FIGURE 10-1. Organizational Relationships for Barrier Materials Testing.

11.0 SCHEDULE AND SUMMARY LOGIC DIAGRAM

Logic diagrams governing the flow of work for each testing activity have been constructed and are found at the end of Sections 5.1.1.1, 5.1.2.1, 5.1.2.2, 5.1.2.3, 5.1.2.4. These have been summarized in Figure 11-1.

A summary schedule for the barrier materials testing has been prepared using Figure 11-1 as a basis and is shown in Figure 11-2. As new data, information, and BWIP programs needs are identified, the logic diagrams and control schedule will be updated.

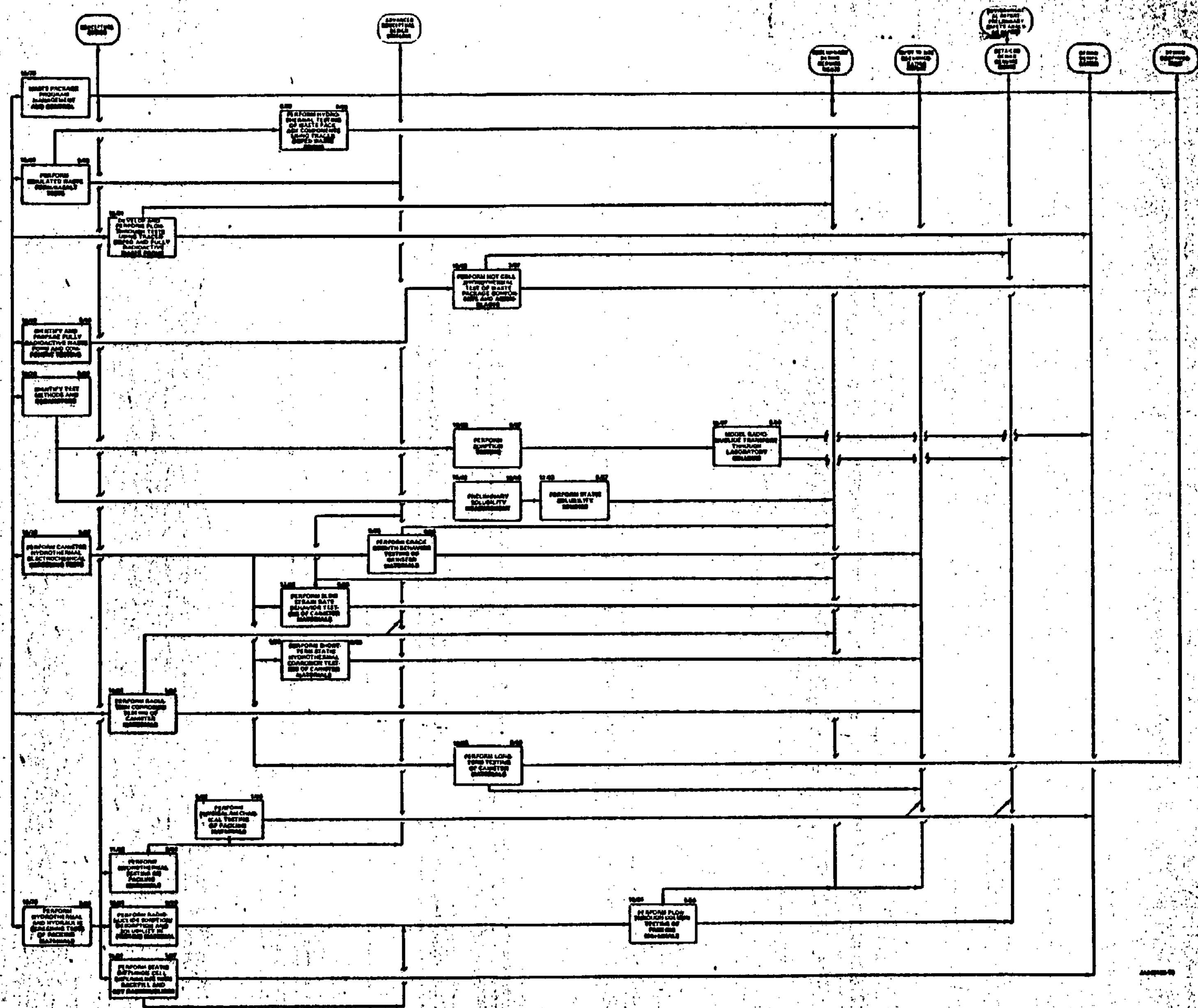


FIGURE 11-1. Waste Package Summary Logic Diagram.

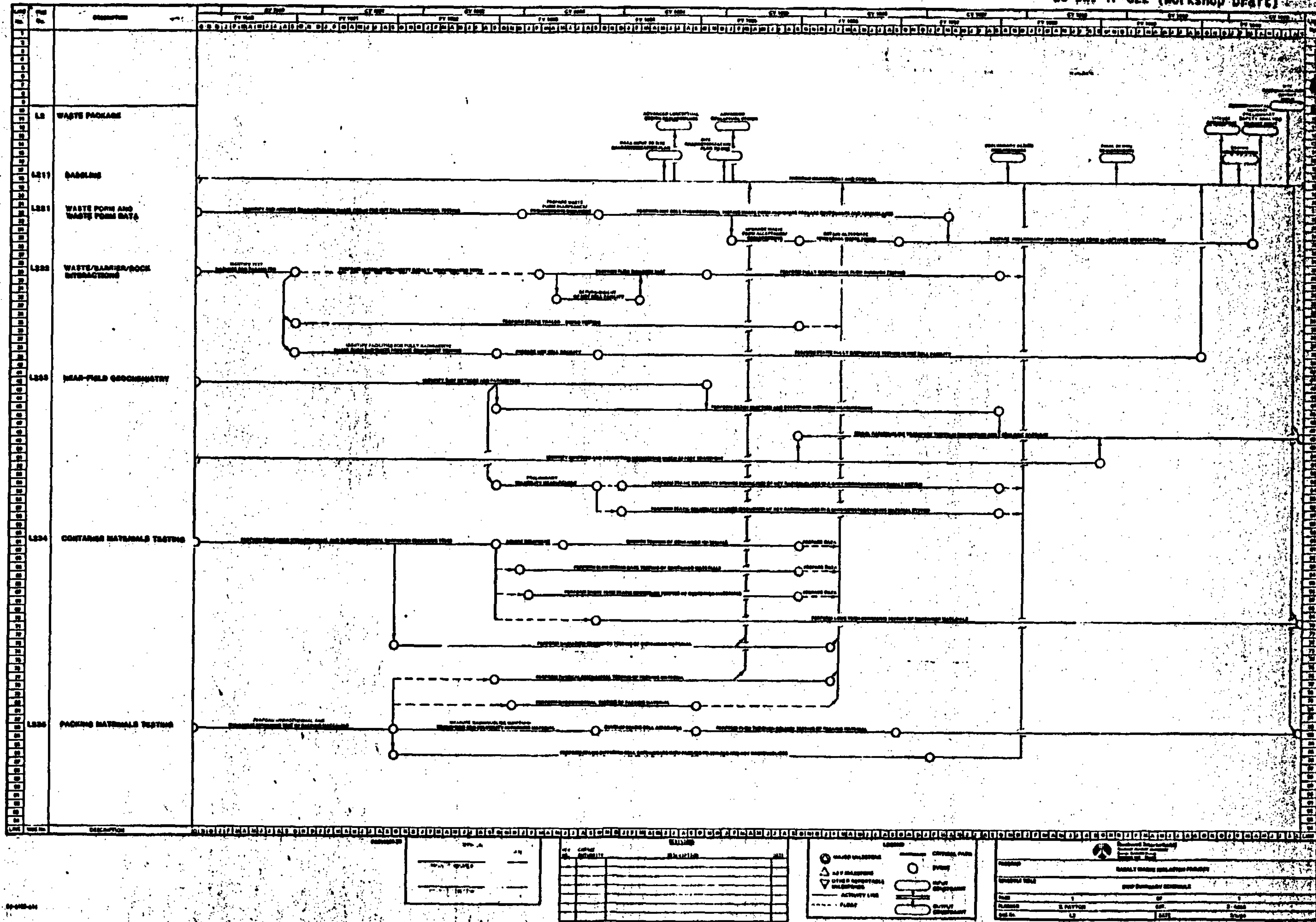


FIGURE 11-2. Waste Package Summary Schedule.

12.0 REPORTS AND MEETINGS

12.1 INTRODUCTION

Progress and performance on materials tests being conducted for the BWIP will be evaluated and reported in the reports and meetings defined below. These meetings and reports will communicate the basic information required for both internal and external control of technical, cost, and schedule performance, and identification of problems requiring management action. All test results destined for release or presentation will be issued as BWIP documents under the authorship of the appropriate BWIP contractors. Technical information generated from contractor tests will not be released to individuals without prior, written approval of the BWIP Director. Technical papers presented at society and technical meetings will be reviewed by the BWIP prior to submittal to DOE-RL for approval. Abstracts for such technical papers must be approved by the BWIP Director prior to commitment to present or write a full paper for a technical society or otherwise-sponsored meeting.

12.2 WEEKLY BRIEFING REPORTS

12.2.1 Contractor Reports

A brief weekly report (about one page) will be prepared by each team leader for subcontracted tasks defined by the BWIP. Two copies of the report will be delivered to the Manager of the Engineered Barriers Department each Friday. The report will document the significant activities affecting project status which occurred during the period. The weekly report will be the principal communication medium for transmitting current information. The report will be categorized into three sections: (1) problems, (2) achievements, and (3) information.

The problems section will report significant conditions that affect testing schedule, quality, or cost. If possible, a reported problem should be accompanied by a proposed solution.

Achievements include the completion of preliminary and final milestones as well as items which are considered to significantly affect the completion of milestones. The information section will report the remaining significant activities.

12.2.2 Rockwell Reports

The requirements for these reports are the same as those stated in Section 12.2.1.

Corrosion studies were performed at the Basalt Materials Research Laboratory in FY 1983 on low-carbon steel (Anatatmula et al., 1983) under conditions closely representing those anticipated in the repository (i.e., with specimens in direct contact with the packing materials). These tests were performed using reference Umtanum flow groundwater (GR-3), whereas the groundwater to be used for BWIP testing in FY 1984 and beyond will be the reference Cohassett flow groundwater (GR-4) representative of the reference repository location. Three low-carbon steels were selected for this purpose: AISI 1006, 1020, and 1025. The effect of groundwater chemistry on the corrosion behavior of low-carbon steel was also investigated. The following anion concentration variations were studied using a Plackett-Burman test design: Cl^- up to 780 mg/L, F^- up to 100 mg/L, $CO_3^=$ up to 120 mg/L, and $SO_4^=$ up to 576 mg/L. Synthetic groundwater was sparged with high-purity argon gas prior to mixing it with packing materials (75 wt% basalt/25 wt% bentonite) for testing purposes. Small pressure vessels (up to 125 mL volume) were loaded in an argon glove box by submerging the specimens in the groundwater-saturated packing materials mixture. The corrosion tests were performed under static, anoxic conditions (<0.1 mg/L O_2 as measured by colorimetric techniques) over the temperature range of 100° to 250°C for periods of up to 6 wk. The low-carbon steels exhibited an average uniform corrosion rate of 8 μm/yr (0.3 mil/yr) at 250°C and 66 μm/yr (2.6 mil/yr) at 100°C assuming linear kinetics during the 4-wk tests. A limited number of corrosion tests were also conducted on Fe9Cr1Mo steel. The Fe9Cr1Mo steel exhibited an average uniform corrosion rate of 1.8 μm/yr (0.07 mil/yr) at 250°C and 2.8 μm/yr (0.1 mil/yr) at 100°C assuming linear kinetics during the 4-wk tests. Under the anoxic conditions of these tests with the specimens in contact with packing materials, the corrosion was independent of the carbon composition for the low-carbon steels. The groundwater chemistry variations that were investigated were found to have no statistically significant effect on the corrosion behavior of low-carbon steel in comparison with the effect of test temperature. The lower corrosion rates exhibited by the steels at 250°C as compared to their behavior at 100°C were attributed to a very adherent layer of iron-rich clay formed on the surface of the steel at 250°C which tended to reduce the rate at which corrosion proceeded. The Fe9Cr1Mo alloy steel specimens exhibited a significantly lower corrosion rate than the low-carbon steel at both 100° and 250°C. Pitting was not detected in any of the specimens.

A 5-mo refreshed autoclave test was also completed in FY 1983 at the Basalt Materials Research Laboratory on Fe9Cr1Mo steel, wrought and cast AISI 1020 steels, and Cupronickel 90-10. The test was conducted under anoxic conditions in basaltic groundwater (9.75 pH, <.05 mg/L oxygen) at 200°C at a low flow rate of 0.02 mL/min. The average corrosion rates were 0.9, 0.9, 1.0, and 1.5 μm/yr (0.035, 0.035, 0.04, and 0.06 mil/yr) for Fe9Cr1Mo, Cupronickel 90-10, cast low-carbon steel, and wrought low-carbon steel, respectively. These corrosion rates were calculated assuming linear kinetics during the 5-mo test. Pitting was not detected in any of the specimens.

The refreshed autoclave corrosion data generated by Westerman (1983a) and the static pressure vessel corrosion data generated at the Basalt Materials Research Laboratory during FY 1983 (Anatatmula, et al., 1983) were summarized and statistically treated by the BWIP (Fish and Anatatmula, 1984) to provide standard deviations for each set of data. While all the tests conducted through FY 1983 are valuable for screening and initial evaluations, longer term, detailed tests on the reference and backup container materials under conditions closely simulating the repository operating and postclosure periods are required to fully characterize the corrosion behavior and understand the mechanisms controlling degradation.

5.1.2.3.5 Planned Testing.

5.1.2.3.5.1 Mechanical Testing. Two areas of concern relative to the mechanical response of a nuclear waste container are the effects of the repository environment on (1) tensile properties of the container material and (2) response of the material to potential materials fabrication flaws under cyclic- and static-load conditions. The objective of the testing in each area will be to determine the environmental effects on these key mechanical properties needed for waste package design. All data will be generated, analyzed, and reported in time to support the completion of work requirements W.2.3.B, W.2.13.B, W.2.16.B, W.2.4.A, and the closure of issues W.2.A and W.2.B.

Slow-Strain-Rate Testing. The environmental effects on the tensile properties of container materials will be determined using a slow-strain-rate test technique. The data generated by this technique include proportional elastic limit, ultimate tensile strength, total elongation, and reduction of area. The test data will provide a relative indication of susceptibility to environmentally assisted cracking (e.g., stress corrosion cracking) for the purpose of comparing container materials. This susceptibility is evidenced by a loss of strength or ductility of the container material in the synthetic groundwater environment in comparison with these same properties measured in an air environment used as a reference. In addition, post-test fractographic analyses will be conducted to visually detect evidence of embrittlement such as a larger percentage of fracture surface exhibiting intergranular or cleavage mode of failure. The slow-strain-rate test is used for comparative purposes only since quantitative environmentally assisted cracking effects cannot be predicted using slow-strain-rate test results that are qualitative with regard to environmentally assisted cracking.

A diagram of an autoclaved slow-strain-rate testing apparatus belonging to the BWIP is shown in Figure 5-11. The test is conducted by straining the specimen to failure at a fixed rate while it is immersed in synthetic basalt groundwater at temperature. The groundwater is pumped through a bed of crushed basalt lying in the bottom of the autoclave to reduce the O_2 concentration. The specimen load and strain rate are continuously recorded. Strain rates of 1×10^{-4}/s to 2×10^{-7}/s are to be employed. Test temperatures to be investigated will be in the range of 50° to $300^{\circ}C$. Since container material comparison is the primary purpose of this testing effort, synthetic Grande Ronde Basalt groundwater will be used with oxygen concentrations and flow rates considered to be conservatively high in comparison with expected repository conditions.

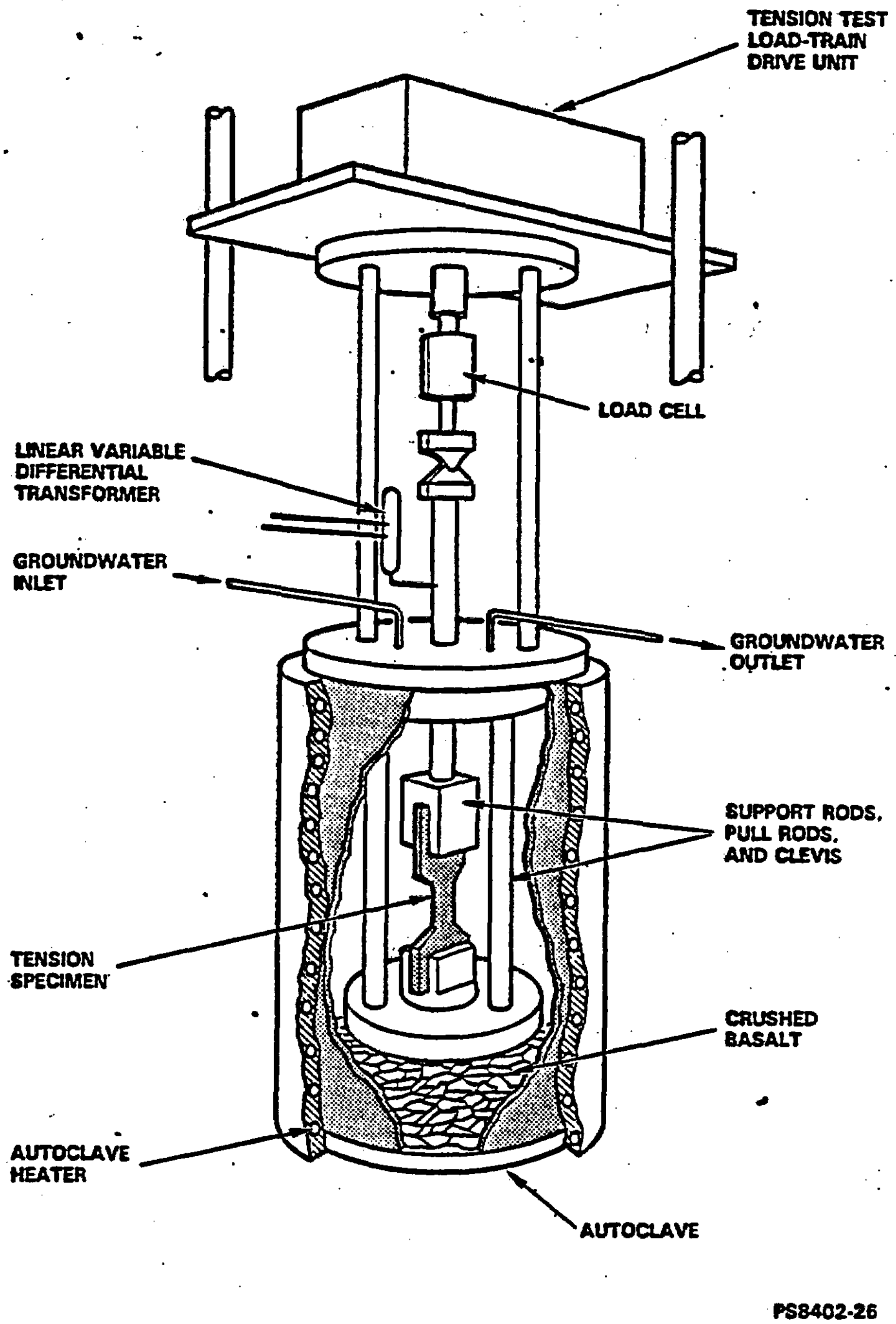


FIGURE 5-11. The Basalt Waste Isolation Project Slow-Strain-Rate Test System.

During FY 1984, slow-strain-rate data will be generated on wrought and cast low-carbon steel, Fe9Cr1Mo steel, and Cupronickel 90-10. Equipment will be procured to conduct tests in a gamma radiation field. During FY 1985, slow-strain-rate data will be generated in a gamma radiation field on low-carbon steel, Fe9Cr1Mo steel, and Cupronickel 90-10. Slow-strain-rate data accumulated during FY 1984 and 1985 will be used to help select the reference container material in time to fabricate waste packages for the Waste Package Materials Degradation Engineering Test to be initiated in October 1986. Data accumulated during FY 1986 will either further confirm or possibly negate the choice of the reference container material.

Crack Growth Testing. Brittle failure of metallic materials in the presence of a static tensile stress and corrosive environment has been widely observed, and its potential must be evaluated in any thorough assessment of container materials behavior. Fracture mechanics will be employed to quantitatively assess the potential for environmentally assisted cracking in candidate container materials under both static- and cyclic-loading conditions in high temperature/high pressure aqueous environments simulating repository conditions.

For this testing, statically loaded fracture mechanics specimens will be used to provide a quantitative assessment of stress-assisted embrittlement phenomena over a range of experimental conditions including applied stress and flaw (crack) size which can be related with a stress intensity factor. The stress intensity factor, K, is directly proportional to the applied stress, to the square root of crack length, and to various geometrical factors. The quantity K_{ISCC} is the stress intensity factor for the onset of crack extension, i.e., cracks can only extend when $K_{applied}$ is greater than K_{ISCC} in the environment of interest. K_{ISCC} can be utilized directly in waste package design and analysis to assure that actual limits on flaw size (e.g., as defined by nondestructive examination) are less than the critical flaw size (i.e., the flaw size for which $K_{applied}$ equals K_{ISCC} for the stress and geometry of interest). Determination of K_{ISCC} at levels above threshold values (K_{th}) established by cyclic-loading techniques (described later) will provide the basis for reasonable assurance that stress/flaw size combinations (using K_{th}) can be utilized as an upper limit in design to preclude the possibility of container cracking for the waste package containment period.

Measurement of K_{ISCC} under static load will be achieved by exposing self-stressed (i.e., bolt-loaded) wedge-opening loading fracture mechanics specimens in an autoclave. Various exposure times will be required since it is often found that the apparent K_{ISCC} in an aqueous environment decreases with increasing exposure time. In this test, crack extension occurs under constant displacement and decreasing load. Measurement of these quantities permits a calculation of K_{ISCC}. If no crack extension occurs, a value of K is defined which is likely less than K_{ISCC}.

Tests will involve the exposure of specimens of each candidate container material in an environment representative of that in a nuclear waste repository in basalt for exposure times of up to 20,000 h. Synthetic Grande Ronde Basalt groundwater (conditioned with crushed basalt and bentonite to simulate groundwaters having passed through the packing materials) will be used to simulate the container environment. Test temperatures of 150° and 250°C will be investigated.

During FY 1983, static load crack growth testing was initiated at 250°C for test durations targeted for 2,000 and 20,000 h. Data from the 2,000-h test will become available in FY 1984. During FY 1984, static load crack growth data will be generated at 250° and 150°C for both the low-carbon steel and the FeCrlMo steel container materials and their weldments to a 2,000-h target test duration. During FY 1985, a 10,000-h test at 150°C will be initiated, and data from the 20,000-h test will become available near the end of the year.

The static load crack growth tests will generate data to provide reasonable assurance that environmental embrittlement phenomena (e.g., stress corrosion cracking) either are or are not likely to be active in the container materials, under conditions expected in a nuclear waste repository in basalt. Data accumulated during FY 1983 and 1984 will also be used to show whether or not allowable stress/flaw size combinations less than an upper limit are obtainable with the container materials for container design.

A quantitative assessment of crack extension will also be made under cyclic loading conditions in high-temperature, high-pressure aqueous environments simulating repository waste package conditions. Since K_{ISCC}, as determined under static loading, may decrease as longer experiments are conducted, it may be very difficult, with the static load data alone, to satisfactorily argue the absence of any cracking over a time period of 1,000 yr. One method of placing more conservative limits on K is to conduct tests using cyclic loading, since it is sometimes found that such fatigue crack extension can occur at K levels below K_{ISCC} in the environment of interest. Although cyclic loading of containers is not expected to occur in the repository, cyclic loading tests provide a basis for establishing K_{th} values for design and materials evaluation, which may be more conservative than K_{ISCC} and thereby add confidence to the position that cracking can be avoided during the containment period of the repository.

Cyclic loading adds significantly to the number of test parameters that must be controlled and possibly varied. The frequency of cyclic loading, the ratio of minimum to maximum stress, and the load waveform are all factors that have been found to be important in producing accelerated fatigue effects in corrosive environments. Evaluation of the effects of high-temperature, high-pressure aqueous environments on cyclic loading behavior will also require a determination of the material response in a reference environment such as air, since fatigue occurs even in the absence of corrosion.

Tests will be conducted in autoclaves containing synthetic Grande Ronde Basalt groundwater, crushed basalt rock, and bentonite. Figure 5-12 shows a schematic of the BWIP cyclic testing apparatus. Tests will be conducted at approximately 11.4 MPa at temperatures between 50° and 300°C. Autoclave features for the cyclic loading tests will include electrical isolation of the specimen from the load train, on-line measurement of dissolved oxygen, pH, water conductivity, specimen potential relative to a reference electrode, and a bypass loop for drawing water samples for additional analysis.

During FY 1983, reference (air) cyclic crack growth data were generated for low-carbon steel (wrought and cast) and Fe9Cr1Mo steel. In addition, autoclaves for conducting cyclic crack growth tests in a groundwater environment at elevated temperatures will be procured and installed. During FY 1984, fatigue crack growth data will be generated in synthetic Grande Ronde Basalt groundwater for wrought low-carbon steel and Fe9Cr1Mo steel. During FY 1985 and beyond, fatigue crack growth data will be developed for weldments of the container materials and to help understand the effects of variables such as gamma radiation, oxygen content, groundwater composition (including CO_3^{-2} ions), and flow rate, etc.

The cyclic crack growth data will provide the basis, in conjunction with the static load data, for establishing a more conservative threshold stress intensity factor (K_{th}) to preclude environmentally assisted cracking of the container. The data will be used in container design by defining allowable stress/flaw size combinations that will provide reasonable assurance that brittle failure of the container will not occur. Data accumulated during FY 1984 through 1986 will be used to confirm the choice of a reference material for container design.

5.1.2.3.5.2 Corrosion Testing. The objective of the corrosion testing effort is to characterize the corrosion behavior of reference and backup container materials, to provide data for predictive models, and to define confidence limits for the extrapolation of the materials behavior to time periods required for containment.

Prior to packing materials emplacement, the container will be exposed to an air environment with potentially high humidity conditions. Since the surface of the container will exceed 100°C at essentially atmospheric pressure, an aqueous liquid phase will not exist on the container surface and, therefore, corrosion is expected to be minimal. However, oxidation of the container material will occur to some extent, and this effect must be understood relative to possible metal loss and subsequent effects on aqueous corrosion after repository closure.

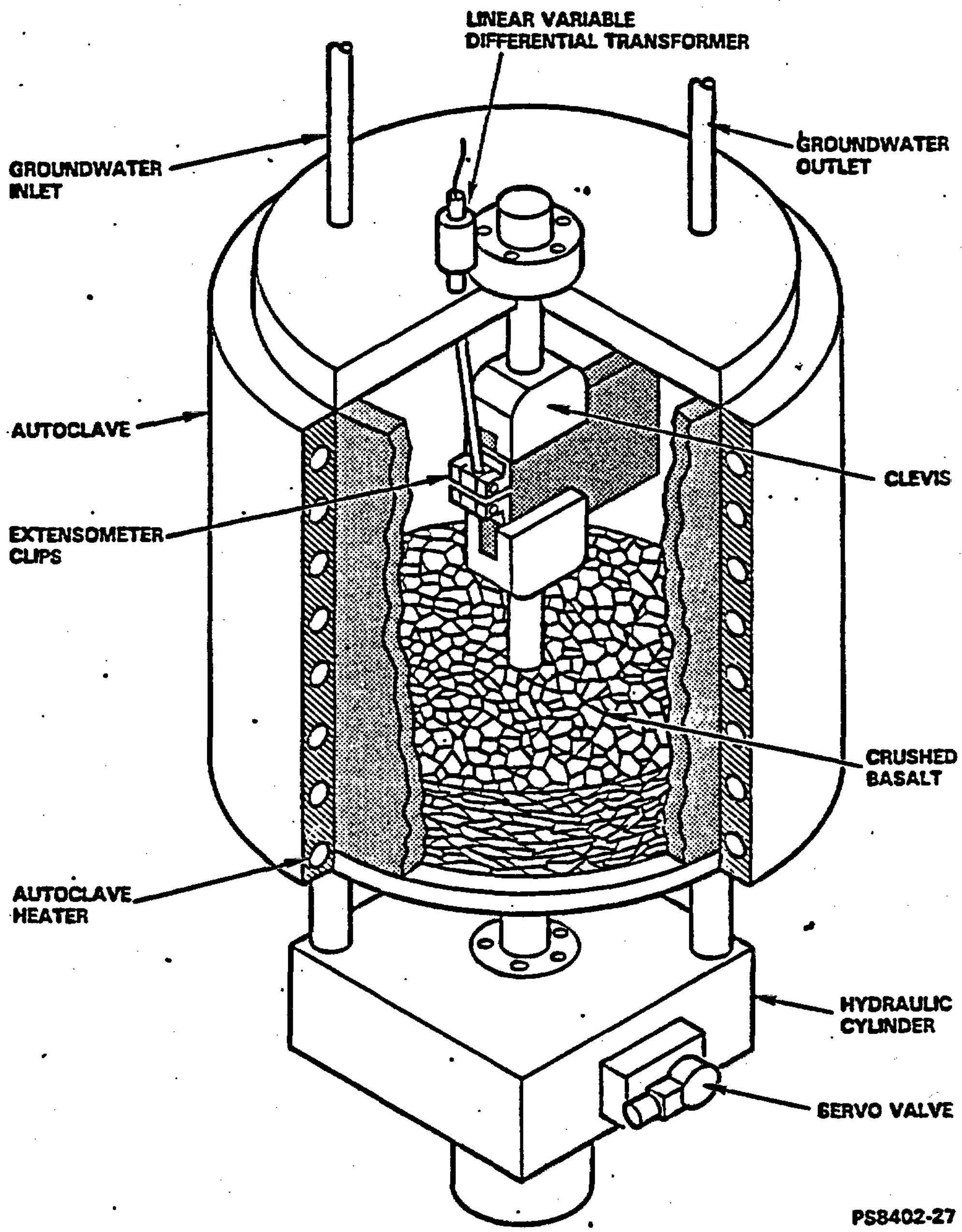


FIGURE 5-12. The Basalt Waste Isolation Project Cyclic Crack Growth Autoclave Test System.

After packing materials emplacement and eventual saturation, the aqueous environment will produce corrosion of the container material by distinctly different mechanisms than those active prior to packing materials emplacement. These degradation mechanisms may include pitting, intergranular, and crevice corrosion as well as uniform corrosion. Bacteria that thrive in reducing groundwater environments may exist to enhance corrosion rates by reducing sulfates (LaQue and Copson, 1965) that assist ferrous sulfide formation (Berry, 1982). The effect of bacterial corrosion in a gamma radiation environment will be investigated by the BWIP. Each of these mechanisms may result in vastly different corrosion rates. The different mechanisms may also produce different corrosion product films. It is essential, therefore, that the film formation behavior and related kinetics of active corrosion mechanisms be understood in order to provide a valid and defensible basis for extrapolation of the corrosion data generated. Corrosion data will be generated, analyzed, and reported in time to support the completion of work requirements W.2.4.A, W.2.3.B, W.2.13.B, W.2.16.B, and the closure of issues W.2.A and W.2.B.

<u>Short-Term Testing</u>. Changes in the Eh, pH, and chemistry of the groundwater that makes contact with the container will be primarily dependent on the temperature, gamma radiation level, and the basalt/bentonite packing material. For testing purposes, the variables of Eh, pH, and groundwater chemistry are interdependent and can vary as any individual variable is controlled. Therefore, the effects of water chemistry, Eh, and pH on corrosion will be studied, using relatively short-term ($\leq$3 mo) tests over a period of 2 yr or more, to provide a basis for assigning conservative levels to these variables to be used in long-term testing efforts. The planning for the short-term tests will be guided by the statistical test design considerations described in Appendix A.

The short-term testing will involve the use of static pressure vessels to contain corrosion specimens and the desired environment as illustrated in Figure 5-13. These enclosed vessels will be heated in an oven to provide a static test environment at temperatures of up to 250°C. The pH levels will be varied in the range of 6 to 10; Eh will be controlled by sparging the groundwater with an inert gas and by the presence of crushed basalt or a packing materials mixture. The effects of variations in groundwater chemistry (Cl^-, F^-, etc.) on the corrosion behavior (uniform, pitting, and crevice corrosion) will be investigated. Bacterial corrosion will also be studied as part of the short-term testing effort. Both wrought and cast forms of the low-carbon steel will be tested as well as weldments of the candidate materials; polished and as-received surface conditions will be evaluated. The corrosion behavior of candidate container materials taken from different heats and produced with varying heat treatments will also be investigated.

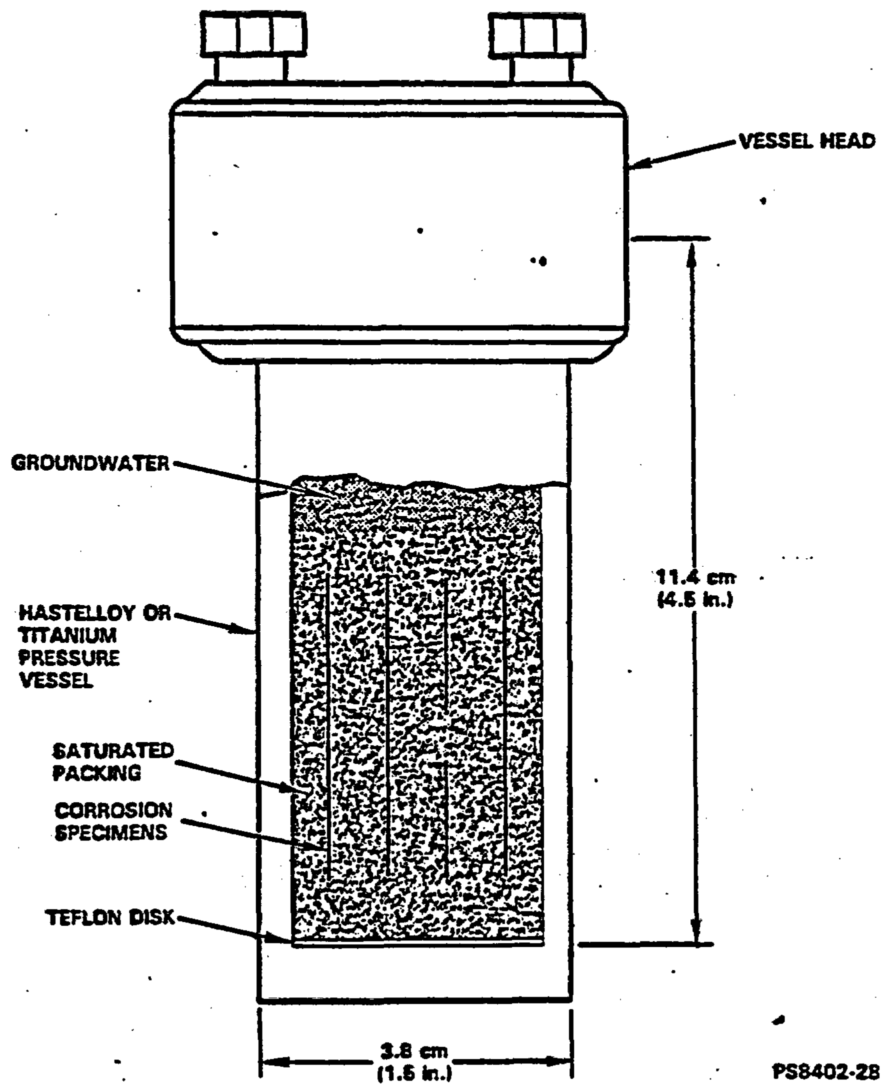


FIGURE 5-13. Schematic of the Basalt Waste Isolation Project Static Pressure Vessel Corrosion Test System.

Electrochemical characterization (anodic and cathodic potentiodynamic scans to measure pitting potentials, etc.) of the candidate container materials will be performed under conditions anticipated at the container surface. The possibility of pitting and pitting incubation times will be determined by monitoring the corrosion potential (volts) in long-term tests (described under "Long-Term Testing"). If warranted by the results of these tests, the corrosion kinetics of pitting in the candidate container materials will be studied intensively using recently developed techniques involving electrochemical polarization of specimens of varying thickness under hydrothermal conditions.

During FY 1983, corrosion data were generated to establish the effects of carbon content and groundwater composition for low-carbon steel in the presence of the reference packing materials. Data generated during FY 1984 will be used to help develop the waste package advanced conceptual design requirement by permitting a better definition of container wall thickness needed to allow for general and preferential corrosion. During FY 1984, corrosion data will be generated to establish the effects of the anticipated hydrothermal environment on weldments for low-carbon steel and the backup materials. Groundwater chemistry effects on Fe9Cr1Mo steel and air/steam/packing materials environments on the reference low-carbon steel will be investigated by short-term testing in FY 1984. Also during FY 1984, pit growth rate studies will be initiated for both the reference and backup material. Potentiodynamic characterization of the container materials will be performed under the hydrothermal conditions anticipated at the container surface. During FY 1985, short-term testing of container materials will be continued with emphasis on air/steam/packing materials testing of the backup materials. Groundwater composition-effect tests will also be initiated in FY 1985 for Cupronickel. Evaluations of bacterial corrosion and the effects of exposure to air/steam on subsequent aqueous corrosion rates are also planned. During the short-term corrosion testing, the composition, growth rate, and stability of the corrosion products will be characterized to assist in the long-term prediction of materials behavior (performance assessment) in the repository environment.

Radiation Testing. The effect of gamma radiation on the corrosion behavior of container materials in a groundwater/packing materials environment must be established. Radiation (primarily gamma) is expected to produce radiolysis of the groundwater and modify its composition. Since the radiation level will vary with time during the container lifetime, it is important to understand the effects of this variable on the corrosion behavior (uniform, pitting, crevice, intergranular, and bacterial, in addition to possible hydrogen embrittlement that may lead to stress corrosion cracking) of the candidate materials.

In order to study gamma radiation effects on the corrosion and possible hydriding of candidate container materials under repository-relevant conditions, an existing ^{60}Co radiation facility at the WHC has been modified to accept high-pressure, high-temperature refreshed autoclaves and static pressure vessels. A schematic diagram of the facility is shown in Figure 5-14. The electrically heated autoclaves and static vessels lie within dry access tubes in the water pool. The autoclave has its own

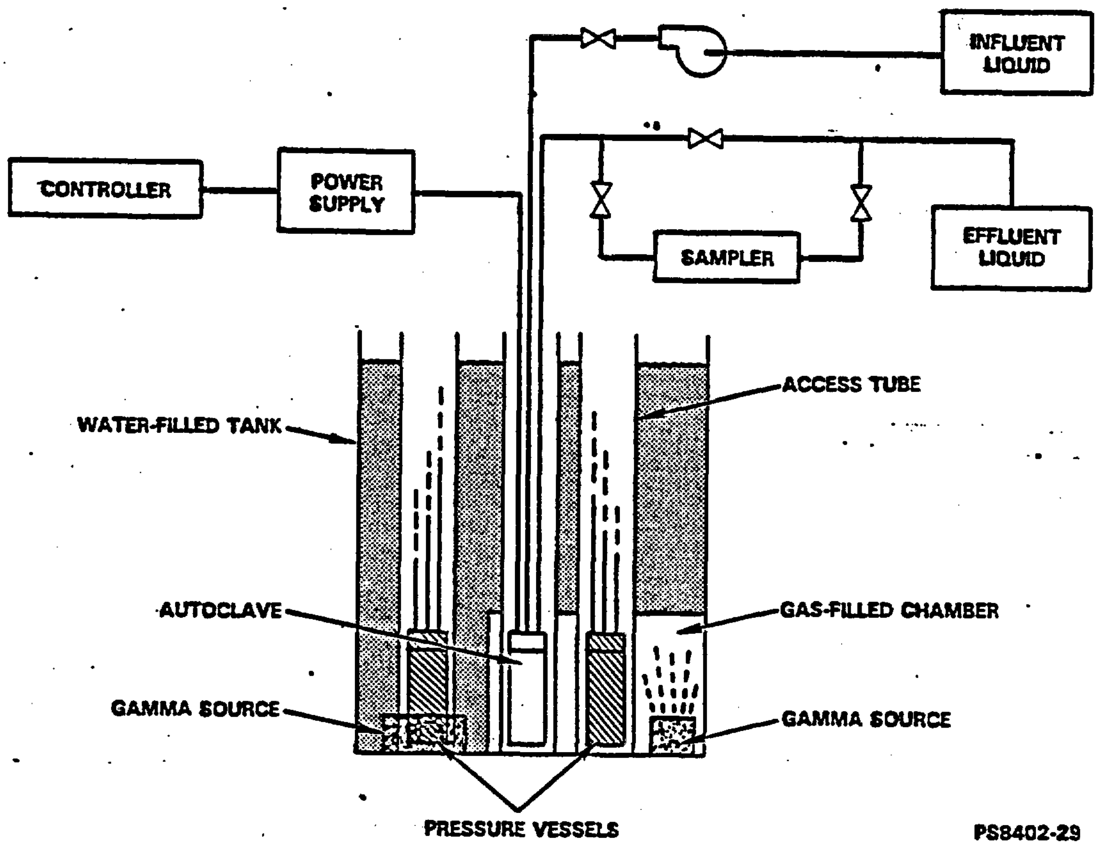


FIGURE 5-14. Schematic of the Radiation-Corrosion Test Facility Used by the Basalt Waste Isolation Project.

independent water inlet, sampling, and effluent system. The system is capable of exposing specimens to synthetic Grande Ronde Basalt groundwater/packing material environments at a maximum temperature of 300°C and a maximum radiation dose rate to the specimen of approximately 3×10^5 rad/h. The synthetic groundwater can be sparged with air or other gases (i.e., argon, methane, etc.) in the source tank. Crushed basalt will be used to precondition the synthetic groundwater before it passes upward (5 mL/h max.) through the autoclave occupied by the specimens. The autoclave has a volume of approximately 1 L. Tests will be conducted in the temperature range of 100° to 200°C at gamma flux levels expected at the container outer surface as well as higher levels for conservatism.

At the end of FY 1983, corrosion data was available for a 13-mo exposure of ferrous alloys at 250°C and on wrought and cast low-carbon steel at 250°C, after a 5-mo exposure to a radiation field with a 3×10^5 rad/h flux rate. Study of the effects of packing materials on the corrosion behavior of container materials will be initiated in FY 1984. The effects of dissolved methane and nitrogen gases on the corrosion behavior of candidate container materials will be initiated in FY 1984. The radiation corrosion testing of cast low-carbon steel, the backup materials, and their weldments in contact with packing materials will continue in FY 1985. The effects of CO_2 gas on the container materials corrosion behavior will also be investigated as test space becomes available. Characterization of the surface corrosion product will be conducted, and the results will be compared with analyses obtained on corrosion product developed without exposure to gamma radiation. This comparison will dictate any changes required in data input to the waste package degradation modeling activity.

Long-Term Testing. Long-term corrosion tests (up to 10 yr) are planned that will provide the essential data base for understanding corrosion mechanisms and extrapolating, with increased confidence, the corrosion rates of the reference and backup container materials through the containment period of the nuclear waste repository in basalt. The data will be generated using air/steam chambers, refreshed 1 L and 1 gal autoclaves, as well as static pressure vessels (also used in short-term tests) set up to simulate as closely as possible the environments that will be experienced by the container in the repository. The hydrologic regime within the waste package is likely to be quite stagnant regardless of the situation in the repository host rock, because of the low permeability and other conditions imposed by the waste package bentonite/basalt packing materials. Furthermore, the water in this area is likely to be present in very low quantities (i.e, pore saturation of the packing materials). Because of this, the water in contact with the exterior surface of the container is very likely to be saturated with corrosion product. This saturation produces a concentration polarization effect and acts to decrease the rate of container corrosion significantly. Incorporation of the packing materials in the test vessels and autoclaves is, therefore, very important for long-term testing.

A schematic diagram of a typical autoclave corrosion test facility used for long-term testing is shown in Figure 5-15. A reservoir contains the groundwater made up to a specified composition and sparged with an inert gas mixture. A positive displacement pump delivers influent water to the autoclave at a very low flow rate (net 5 mL/h max.). The water flows through a bed of crushed basalt at an elevated temperature prior to contact with the corrosion specimens. Static autoclaves will be used to monitor corrosion potential (volts) and instantaneous corrosion rates using polarization resistance techniques in long-term tests. Weight loss measurements at the end of the electrochemical tests will be used to calibrate the data collected during the test.

It has been found that a bed of crushed basalt in the bottom of an autoclave will decrease the oxygen concentration level of water from 8 mg/L to levels approaching 0.3 mg/L at the autoclave outlet, at 250°C (Westerman, 1983a) even at flow rates of 35 mL/h. This was attributed to the reducing effects of large amounts of divalent iron present in the basalt. Additional reduction in the oxygen content of the water will occur if the water is sparged with an inert gas as previously noted, if flow rates are reduced, and if the packing material is placed around the corrosion specimens. This procedure should reduce the Eh to values close to those expected to exist in a sealed nuclear waste repository at basalt.

When the desired test duration has been achieved, the specimens will be removed and visually examined. Selected specimens, generally triplicates or quadruplicates, will be stripped of their corrosion product films by immersion in a formaldehyde-inhibited acidic cleaning agent. The specimens will be weighed, and the weight loss converted to metal penetration depth. Selected companion specimens will also be prepared for X-ray diffraction, and metallographic and scanning transmission electron microscopy examination to characterize the corrosion product films as a means of understanding the active corrosion mechanisms.

Time and temperature are the primary variables by which corrosion will be characterized in the long-term testing efforts. All other variables will be controlled either by the simulated environment (i.e., basalt, packing materials, etc.) or by deliberate adjustments dictated by short-term testing results (i.e., groundwater chemistry). The waste package design schedule allows only about 5 yr of testing to generate corrosion rate data for the development of waste package detailed (final) design criteria in FY 1990. Long-term testing in autoclaves, static pressure vessels, and air/steam chambers will continue on the selected container material beyond this time frame (durations of up to 10 yr) through the licensing phase of the repository to provide increased confidence and confirmation of previously developed container degradation models. Test temperatures in the 50° to 300°C range will provide a basis for establishing the dependence of corrosion on temperature.

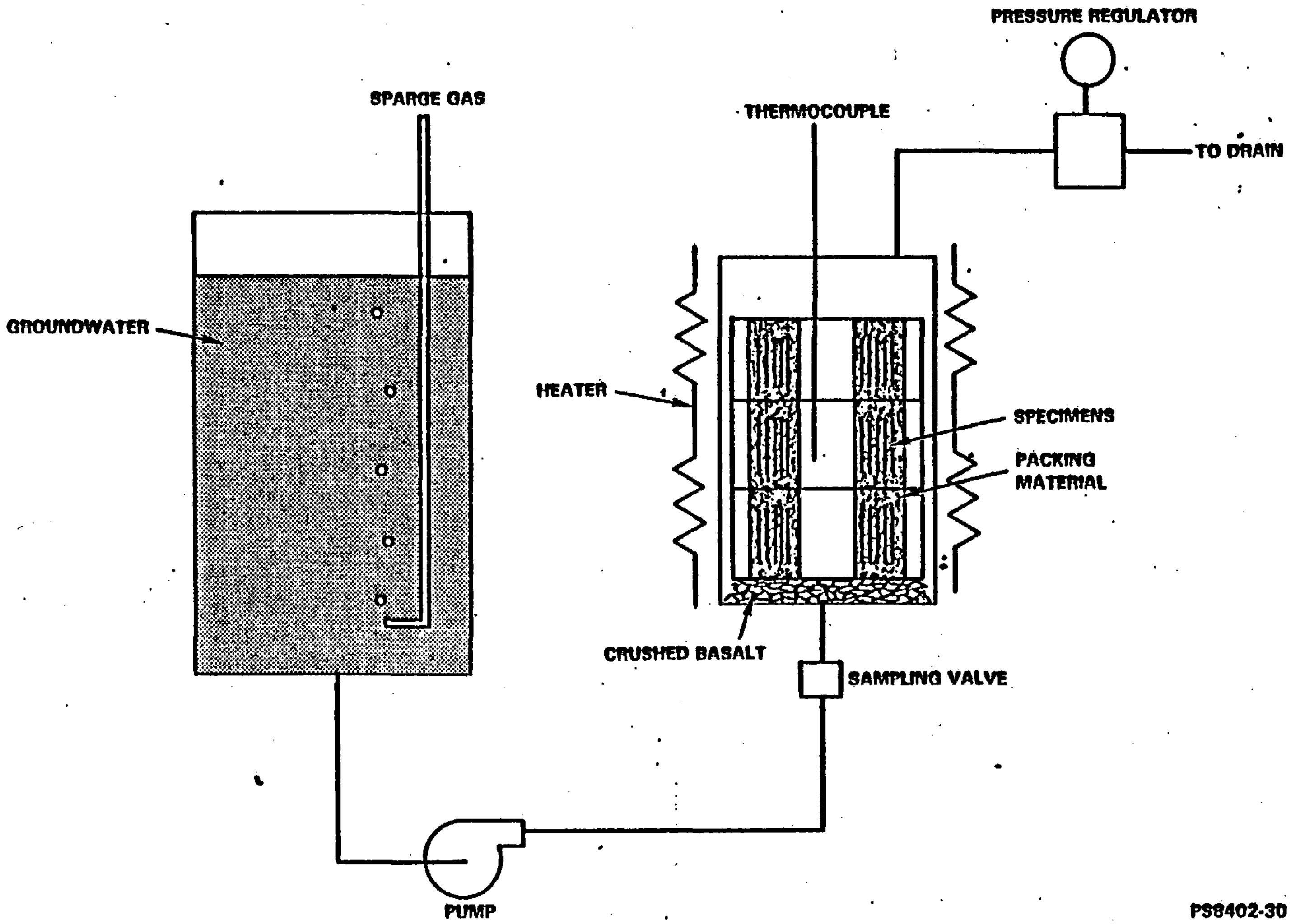


FIGURE 5-15. Schematic of the Basalt Waste Isolation Project Long-Term Autoclave Corrosion Test System.

Three ferrous alloys (ductile iron, Fe2-1/2Cr1Mo, and Fe1-1/4Cr1/2Mo) have been subjected to corrosion tests at the PNL. These tests, being conducted under slightly oxic conditions, will be continued for the BWIP through FY 1983. By the end of FY 1983, ferrous alloy corrosion data will be available for a test duration of 17 mo. Five months refreshed autoclave corrosion data on low-carbon steel, Fe9Cr1Mo, and Cupronickel 90-10 were also obtained in FY 1983. During FY 1984, long-term corrosion tests will be initiated on wrought and cast low-carbon steel and the backup materials in air/steam chambers and with packing materials in Parr pressure vessels and autoclaves over the range of temperatures 50° to 300°C. Also initiated in FY 1984 will be the monitoring of corrosion potential (volts) as a function of time to establish the likelihood of pitting and pitting incubation times for the container materials. During FY 1985 and 1986, corrosion data will continue to be generated on the container materials to provide a basis for developing and refining container degradation models for extrapolating the behavior and for statistically defining confidence limits on the corrosion behavior of container materials. This will require investigation of the corrosion product film to understand its nature and behavior as well as statistical analysis of the data generated. All testing beyond FY 1987 will be limited to the selected reference container material and will be conducted for time periods of up to 10 yr to confirm and increase confidence in the predictive models developed to describe container behavior.

Preliminary corrosion correlations (Fish and Anatatmula, 1984) were developed on the basis of applicable data generated through FY 1983. The correlations provide predictive models for both low-carbon steel and Fe9Cr1Mo steel on a preliminary basis only. Correlations will be developed for Cupronickel 90-10 as applicable data become available. Modifications or possible replacement of the models will occur as more data are generated and evaluated and judgment dictates such action. Quantitative reliability analysis of the data to quantify uncertainties will provide a basis for establishing design corrosion allowances and for describing the time distribution of container failures for performance assessment purposes.

5.1.2.3.6 Logic Diagram. The container materials data required to support waste package design and performance assessment must be generated in a manner consistent with the design and performance assessment schedules. A logic diagram showing the relationship between the container materials studies and input to the design and performance assessment efforts is presented in Figure 5-16.

5.1.2.4 Packing Materials Testing.

5.1.2.4.1 Introduction. To design a waste package packing materials component and predict its long-term performance, data are needed that describe the physical and chemical properties of the packing materials and the interactions between the packing materials, host rock, and other waste package components in the presence of groundwater. These data must describe material strength properties, mass and heat transport properties, and chemical properties of the packing materials so that an effective packing materials can be selected for waste package design and their long-term

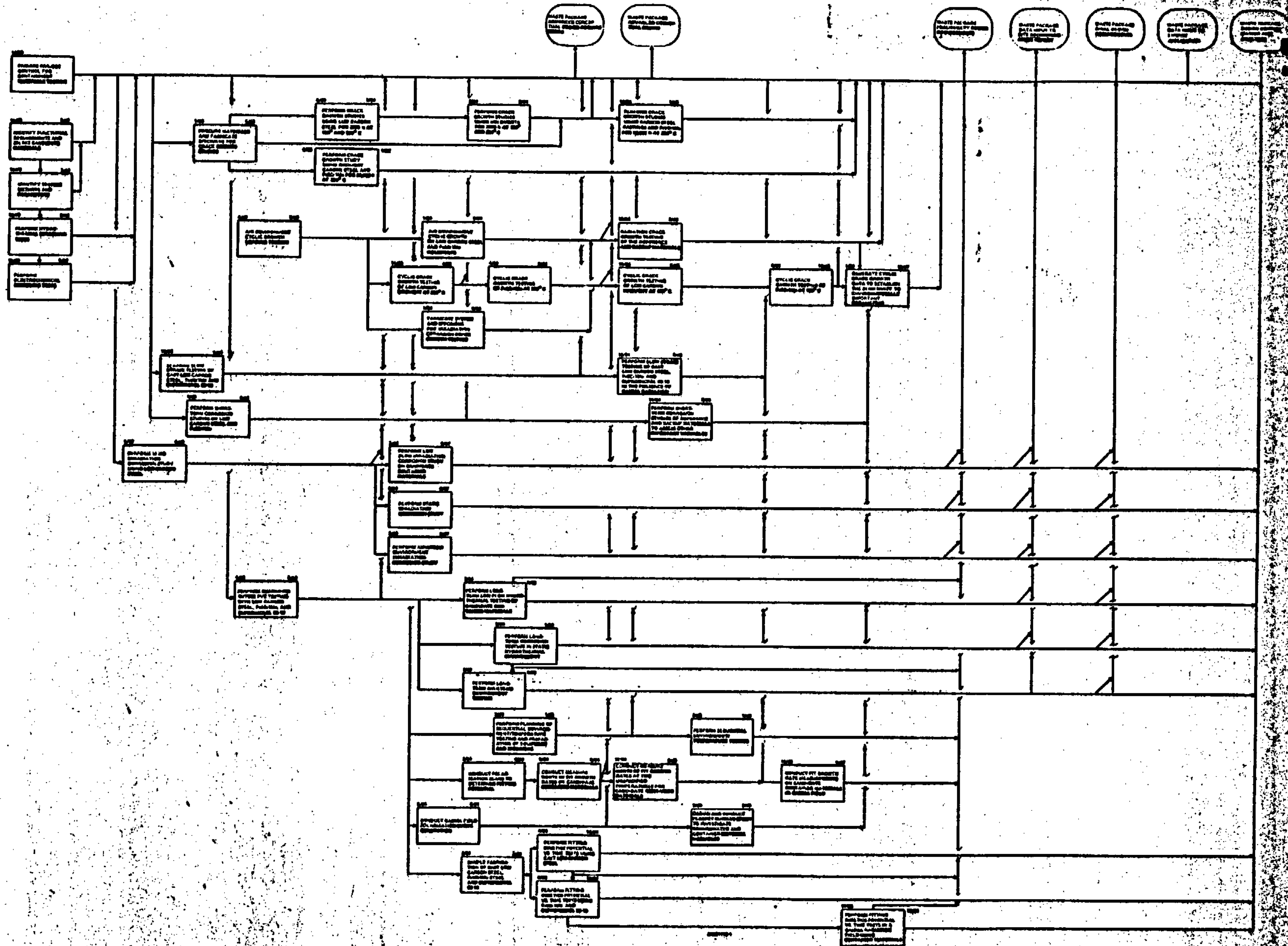


FIGURE 5-16. Containment Materials Testing Logic Diagram.

behavior can be predicted. The predicted behavior can then be compared with applicable regulatory criteria for repository licensing purposes. The regulatory criteria will most likely be stated as limits on release rates of radionuclides from the waste package and/or repository.

This section of the BMTP will describe the tests required to obtain waste package packing materials data that are needed for design and to predict radionuclide release rates from the waste form through the packing materials into the disturbed basalt zone.

A knowledge of the key hydrothermal interactions between waste package components and radionuclides in the near-field environment are needed to predict radionuclide release rates into the basalt. The following parameters will have the greatest effect on the hydrothermal reactions that will occur in the packing materials: (1) the temperature range over which the packing materials is saturated with groundwater, (2) groundwater residence time, (3) water flow rate through the packing materials, (4) groundwater chemical composition, pH, and Eh, and (5) the packing materials composition. During the design life of the waste package, these parameters will change, with the most important change being the decrease in temperature with time as radioactive decay occurs. The decrease in temperature will cause changes in groundwater composition, changes in the rate of hydrothermal reactions, and changes in the packing material phase assemblages. These changes will, in turn, affect the container corrosion, waste form dissolution, and radionuclide transport through the packing materials.

Development of an adequate packing materials test matrix is governed by two major goals. The first goal is to determine experimentally the likely geochemical environment of the waste package packing materials as a function of time so that the effect of changes in temperature, groundwater composition, and packing materials composition on packing materials performance (e.g., minimization of radionuclide transport, container corrosion, and groundwater transport through the packing materials) can be determined. This goal is accomplished primarily through hydrothermal experiments completed over an appropriate range of temperatures under static or low flow conditions with simulated groundwater, crushed basalt, and sodium bentonite. Analyses of experimental solutions and solids provide the necessary information to gage the range of expected geochemical conditions in the packing materials as a function of time. The second goal is to measure the packing materials physical properties over the range of expected repository conditions (e.g., temperature, groundwater, and packing materials composition). These properties include thermal and hydraulic conductivity and groundwater and radionuclide dispersion/diffusion coefficients. These data will be used to accurately predict the capability of the packing materials to minimize container corrosion and radionuclide release from the waste package to the host environment. A more detailed discussion of the primary packing materials tests described above and the relevance of the data to design and performance assessment is given in Section 5.1.2.4.4.

5.1.2.4.2 Objective and Justification. The objective of the packing materials testing effort is to provide sufficient data on the candidate packing materials exposed to the simulated environment of a nuclear waste repository in basalt to assess their ability to meet packing materials design and the NRC performance objectives. The data gathered in this effort are required to (1) recommend reference packing materials for waste package design, (2) define design-related thermal, mechanical, physical, and composition limits, and (3) predict the long-term performance of these materials under repository conditions.

5.1.2.4.3 Summary of Data Needs. The data required to describe the behavior of packing materials may be divided into five categories:

1. Groundwater transport characteristics

2. Strength of materials

3. Heat transport characteristics

4. Radionuclide transport characteristics

5. Hydrothermal reactivity.

Table 5-16 summarizes the data needs in each category of packing material testing, the variables to be measured and/or controlled, and the application of these data to waste package design and performance assessment. A description of the testing techniques required to obtain the data for each category follows. These tests, the range of variables for each test, and analytical techniques required are summarized in Table 5-17.

5.1.2.4.4 Summary of Testing to Date. Preliminary test results have been collected on several packing material properties. The available data and their implications are summarized below. Preliminary hydrothermal testing results for the basalt/sodium bentonite/simulated groundwater system suggest that the mineral alteration observed (e.g., formation of smectites, zeolite, and silica phases) will enhance radionuclide retardation and lower packing materials porosity and permeability (Wood et al., 1982). Experimental evidence to date also suggests that the conversion of bentonite to illite is not significant because (1) the potassium required for this reaction is partitioned into other alteration phases in addition to bentonite (e.g., zeolite, iron-smectite, potassium-feldspar), (2) the kinetics of smectite conversion to illite appear to be quite slow at expected hydrothermal temperatures ($\leq 150^{\circ}C$) (Howard and White, 1981), and (3) the source of potassium in the glassy mesostasis of basalt is limited (e.g., 2.5 to 5.5 wt% K_2O in the Umtanum flow (Allen and Strope, 1983)). Consequently, loss of low hydraulic conductivity and swelling potential is not likely to occur. The implication, therefore, is that hydrothermal interactions should not degrade packing materials performance with time.

TABLE 5-16. Summary of Data to be Obtained from Packing Material Interaction Testing. (Sheet 1 of 3)

Data category	Data produced (units)	Measured or controlled parameters	Application to waste package design performance assessment
1. Groundwater transport characteristics	A. Hydraulic conductivity (m/s)	Temperature, bulk density, clay/basalt ratio, confining pressure, hydraulic head gradient (pore pressure and back pressure)	Hydraulic conductivity values determine groundwater flow rates in the waste package. These are needed to predict the movement of water and radionuclides and to predict temperatures when mass and heat transport are coupled.
	B. Diffusion coefficients of groundwater (m^2/s)	Temperature, bulk density, clay/basalt ratio, confining pressure, hydraulic head gradient (pore pressure and back pressure)	Dispersion coefficient values determine the amount of mixing or spreading of moving groundwater. At low flow velocities, groundwater transport over short distances is dominated by diffusion. Both coefficients are needed to predict groundwater movement in backfill.
2. Resaturation characteristics	Resaturation temperature and time, vapor hydraulic conductivity, swelling pressure, moisture content profile	Temperature bulk density, clay/basalt ratio, confining pressure, swelling pressure, hydraulic head gradient (pore pressure and back pressure)	Resaturation temperatures and time will determine the time after repository closure and the temperature range over which container corrosion, waste form dissolution, and radionuclide transport can be expected to occur. These data will allow a more accurate prediction of long-term waste package performance.
3. Heat transport characteristics	A. Thermal conductivity (W/(m-°K)	Temperature, bulk density, clay/basalt ratio, water content	Thermal conductivity values determine the rate at which heat from the container can be dissipated through the backfill. These data are needed to predict temperatures in the waste package and to predict water movement when mass and heat transport are coupled.

TABLE 5-16. Summary of Data to be Obtained from Packing Material Interaction Testing. (Sheet 2 of 3)

Data category	Data produced (units)	Measured or controlled parameters	Application to waste package design performance assessment
4. Radionuclide transport characteristics	A. Radionuclide retardation factors (unitless number)	Radionuclide oxidation state and concentration, temperature, bulk density, clay/basalt ratio, confining pressure, flow rate, solution composition	Radionuclide retardation factor deter- the migration velocity of a given radionuclide relative to the velocity of groundwater. This can also be used to estimate effective radionuclide coefficients. The retardation factor is needed to predict release rates for radionuclides from the waste package.
	B. Effective diffusion coefficient (m^2/s)	Radionuclide concentration and oxidation state, bulk density, temperature, clay/basalt ratio, solution composition	For situations in which groundwater flow velocities are very slow, mass transport occurs by diffusion. Effective diffusion coefficients are required to predict the movement of radionuclides through the waste package under stagnant groundwater conditons and, thus, for predicting radionuclide release rates.
	C. Radionuclide distribution coefficients/(m^3/kg) and sorption equations (isotherms)	Radionuclide concentration and oxidation state, clay/basalt ratio, temperature, solution composition	The Kd value under ideal conditions determines the retardation factor. For highly sorbed radionuclides, direct measurement of retardation factors may be impossible; therefore, Kd values or other sorption equations (sorption isotherms) for these radionuclides are needed to estimate their retardation factors.
5. Hydrothermal reactions (chemical stability)	A. Alteration products	Temperature, solution/solid ratio, backfill composition, pressure, solution composition, gamma radiation dose	The alteration products that form during hydrothermal reactions of groundwater and backfill indicate the chemical stability of candidate backfills. The kinds of alteration products and amounts formed will effect radionuclide retardation factors and diffusion coefficients, backfill porosity, bulk density, and hydraulic conductivity. These data are required to determine the stability of candidate backfill materials, groundwater transport, and radionuclide transport properties of backfill.

TABLE 5-16. Summary of Data to be Obtained from Packing Material Interaction Testing. (Sheet 3 of 3)

Data category	Data produced (units)	Measured or controlled parameters	Application to waste package design performance assessment
	B. Groundwater composition	Temperature, solution/solid ratio, backfill composition, pressure, initial solution composition, gamma radiation dose	The groundwater chemical composition from hydrothermal reactions of groundwater and backfill will determine radionuclide retardation factors and diffusion coefficients, as well as container corrosion rates. It will also determine the solubilities of radionuclides in the waste package. These data are required to predict the release of radionuclides from the waste package and to evaluate the container lifetime.
6. Strength of materials	A. Shear strength (MPa)	Temperature, bulk density, clay/basalt ratio, confining pressure, pore pressure	The shear strength of backfill determines its bearing capacity or its ability to support the waste form and container should the original support system fail. These data are required mainly for design criteria.
7. Strength of materials (continued)	B. Swelling pressure (MPa)	Temperatue, bulk density, clay/basalt ratio, confining pressure, pore pressure	The swelling pressure determines whether opened fractures in rock walls or voids in the backfill can be filled and low premeabilities maintained in the waste package. The swelling pressure for selected backfill candidates is required for design criteria development to insure that the container is not damaged by the swelling clay on hydration of the backfill.

TABLE 5-17. Summary of Test Techniques Planned for Packing Material Testing. (Sheet 1 of 3)

Test technique	Test equipment	Data produced	Range of parameters	Required analytical
1. Flowthrough column; low temperature, low pressure	Plexiglass column, gas-pressurized influent reservoir	A. Hydraulic conductivity	Temperature, ambient (20° to 25°C); pore pressure, 0 to 0.5 MPa; clay to basalt ration 1:3 by weight; bulk density 1.7 to 1.9 g/cm^3	Flow rates, pressure gradient determinations
		B. Diffusion/dispersion coefficients of water and poorly sorbed elements (nonradioactive tracers)	Temperature, ambient (20° to 25°C); pore pressure, 0 to 0.5 MPa; tracer concentration, 1 to 10 mg/L or solubility limit; clay to basalt ratio 1:3 by weight; bulk density 1.7 to 1.9 g/cm^3	Sample volume determinations, tracer concentration in effluent with ICP, IC, AA, and HPLC for nonradioactive tracers
		C. Retardation factors for poorly sorbed elements (nonradioactive tracers)	Temperature, ambient (20° to 25°C); pore pressure, 0 to 0.5 MPa; tracer concentration, 1 to 10 mg/L or solubility limit; clay to basalt ratio 1:3 by weight; bulk density 1.7 to 1.9 g/cm^3	Sample volume determinations, tracer concentration in effluent with ICP, IC, and AA for nonradioactive tracers
2. Flowthrough column; high pressure, medium temperature	Existing high pressure permeameter	A. Hydraulic conductivity	Temperature, 60° to 90°C; pore pressure, 0 to 10 MPa; bulk density, 1.7 to 1.9 g/cm^3; confining pressure, 0 to 10 MPa; clay to basalt ratio, 1:1 and 1:3	Flow rates, temperature, pressure instrumentation
		B. Diffusion/dispersion coefficients of water and poorly sorbed elements (nonradioactive tracers)	Temperature, 60° to 90°C; pore pressure, 0 to 10 MPa; bulk density, 1.7 to 1.9 g/cm^3; confining pressure, 0. to 10 MPa; clay to basalt ratio, 1:3 by weight; tracer concentration, 1 to 10 mg/L. or solubility limit	Same as 1.B plus temperature and pressure instrumentation
		C. Retardation factors for poorly sorbed elements (nonradioactive tracers)	Same as 2.B	Same as 1.C plus temperature and pressure instrumentation
	High pressure permeameter with load cell and rigid sleeve	D. Swelling pressure	Same as 2.A, no confining pressure	Temperature and pressure instrumentation

TABLE 5-17. Summary of Test Techniques Planned for Packing Material Testing. (Sheet 2 of 3)

Test technique	Test equipment	Data produced	Range of parameters	Required analytical
3. Flowthrough column; high temperature and high pressure	Triaxial cell with confining, pore and back pressure pumps under computer control	A. Hydraulic conductivity	Temperature, 100° to 250°C; pore pressure, 10 MPa; bulk density, 1.7 to 1.9 g/cm³; confining pressure, 0 to MPa; back pressure, 0 to 10 MPa, clay to basalt ratio, 1:1 and 1:3 by weight	Same as 2.A
		B. Swelling pressure	Same as 3.A	Same as 2.A
		C. Resaturation temperature, vapor hydraulic conductivity, swelling pressure, moisture content profile	Same as 3.A	Same as 2.A
		D. Shear strength	Same as 3.A	Sample deformation (rate of change in sample volume)
		E. Alteration products	Same as 3.A	XRD, SEM, microprobe, optical microscopy
	Modified triaxial cell to allot sampling of effluent	Same as 3.A though 3.E plus F. Groundwater composition	Same as 3.A	ICP, IC, and AA
		G. Diffusion/dispersion cofficients of water and poorly sorbed elements (nonradioactive tracers)	Same as 3.A plus tracer concentration 1 to 10 p/m	Same as 3.F plus HPLC
		H. Retardation factors of poorly sorbed elements (nonradioactive tracers)	Same as 3.G	Same as 3.F
	Permeameter modified for high-temperature radio-tracer tests	I. Retardation/diffusion of low to high Kd radionuclides J. Alteration products K. Groundwater composition	Same as 3.A plus temperature 60° to 50°C	Analysis of radionuclides on solids or stripping techniques and analysis of removed radionuclides. Analysis of radionuclides in effluent solutions.

TABLE 5-17. Summary of Test Techniques Planned for Packing Material Testing. (Sheet 3 of 3)

Test technique	Test equipment	Data produced	Range of parameters	Required analytical
4. Heat transport measurement	Thermal conductivity apparatus (Woodward and Clyde subcontract)	A. Thermal conductivity of dry backfill	Temperature, 60° to 250°C; bulk density, 1.7 to 1.9 g/cm^3; clay to basalt ratio, 1:3 and 1:1 by weight; confining pressure	Rate of change in sample temperature
	Thermal conductivity apparatus (outside contractor)	B. Thermal conductivity of saturated backfill	Same as 4.A plus capability for saturated material	Same as 4.A
5. Static column	Diffusion cell and furnace/oven temperature controls	A. Diffusion coefficients (alpha/beta emitters)	Temperature, 60° to 150°C; bulk density, 1.7 to 1.9 g/cm^3; clay to basalt ratio, 1:1 and 1:3 by weight; tracer concentrations, 10^2 to 10^3 pCi/g; confining pressure: vapor pressure at temperature of experiment.	Accurate sectioning of core. Liquid scintillation for α or β detection. Stripping techniques to remove tracer from solid. Surface barrier detection for α
		B. Diffusion coefficients (X-ray/gamma emitters)	Same as 5.A except tracer concentrations required may be one or two orders of magnitude higher	Accurate sectioning of core. NaI(Tl), Ge(Li) and HPGe detectors, with NBS reference material for solids. Stripping techniques and radioanalytical procedures for removed tracers
6. Batch interactions (hydrothermal reactions and chemical stability)	Dickson autoclaves, cold seal pressure vessels	A. Alteration products	Temperature, 100° to 300°C; clay to basalt ratio, 1:1 to 1:3; confining pressure: vapor pressure of water at temperature up to 30 MPa	Same as 3.E
		B. Groundwater composition	Same as 6.A	Same as 3.F
		C. Sorption equations (radioactive tracers)	Same as 6.A	Same as 5.A and 5.B without sectioning core

Note: AA = Atomic adsorption
IC = Ion chromatography
ICP = Induction coupled plasma
HPLC = High pressure liquid chromatographic
NBS = National Bureau of Standards
SEM = Scanning electron microscope
XRD = X-ray diffraction

Another potential mechanism for packing materials degradation is the dehydration of bentonite early in waste package history at peak temperatures. Irreversible loss of structural water in the clay at a high temperature will result in loss of swelling capacity and lower permeability. Recent dehydration experiments show that loss of structural water does not occur at 370°C or below even after a year of continuous heating. These data suggest that the current waste package design temperature limit of 300°C should ensure that irreversible dehydration will be eliminated as a packing material performance degradation mechanism.

Preliminary experiments have been completed at 25°C to determine the hydraulic conductivity of 75% crushed basalt/25% bentonite mixtures (presently the reference packing material composition) as a function of density. The data indicate that hydraulic conductivity decreases with increasing density but, within experimental error, is independent of temperature up to 90°C (Wood et al., 1984). The measurements indicate that hydraulic conductivities of $\leq 1.0 \times 10^{-8}$ cm/s can be achieved at packing materials densities ≥ 1.7 g/cm^3. Preliminary mass transport modeling in the waste package indicates that a hydraulic conductivity $\leq 1.0 \times 10^{-8}$ cm/s should be sufficient to ensure diffusional control of mass transport. A density of 1.7 g/cm^3 is approximately 55% to 60% of theoretical density, and packing materials can probably be emplaced at that density. Other tests have been completed with sodium bentonite alone, which have shown that exposure to dry conditions at 300°C for 6 mo has little effect on the hydraulic conductivity and swelling pressure of pure bentonite when rehydrated at room temperature (Bradley et al., 1983). These data indicate that if the maximum waste package backfill temperature does not exceed 370°C, then any dehydration fractures formed in the backfill during the thermal period will heal by swelling as saturation occurs at a lower temperature.

Swelling tests of pure bentonite at densities of 1.4 to 2.2 g/cm^3 and temperatures between 20° and 90°C have yielded swelling pressures from 5 to 50 MPa (Pusch, 1980). Dilution of bentonite with crushed basalt, however, will reduce the effective density of bentonite to ≤ 1.4 g/cm^3. Therefore, swelling pressures on the order of 5 MPa or less are expected for 1:1 and 1:3 mixes of bentonite with basalt at total bulk densities of 1.7 to 1.9 g/cm^3 (Taylor et al. 1980). Thus, basalt/bentonite backfill mixtures should have sufficient swelling potential to fill voids within the backfill and to penetrate larger fractures in the borehole wall without collapsing the container, which is conceptually designed to withstand no more than 11.3 MPa of compression (AESD, 1983).

An extensive number of batch sorption tests on crushed basalt, sodium bentonite, and zeolites have been completed from 60° to 150°C under oxidizing and reducing conditions (Ames and McGarrah, 1980; Salter et al., 1981a; Salter et al., 1981b; Ames, 1981). These studies have shown that most radionuclides are more readily adsorbed in a reducing environment. Studies of sorption and desorption kinetics initially under reducing conditions indicate that ^{99}Tc, ^{237}Np, ^{238}U, and ^{79}Se either precipitate from solution or are highly sorbed on solid surfaces. In most instances, the mechanism cannot be easily identified, but the effects are the same (e.g., low radionuclide mobility). Radionuclide concentrations decrease in the presence of bentonite and basalt from one to two orders of magnitude or more below their initial concentrations in a reducing environment. Iodine and perhaps carbon are exceptions in that they are both mobile and are not significantly removed from solution by precipitation or sorption under reducing conditions. These preliminary results indicate that the packing material, through interaction with groundwater, appears to maintain a highly reducing and highly sorptive environment that will substantially retard the release of radionuclides from the waste package into the host rock. It should be noted, however, that these results are preliminary and involve the use of hydrazine to achieve a reducing environment. Further testing is in progress either to determine the effects of hydrazine on radionuclide behavior or to complete parallel experiments without hydrazine so that a more accurate simulation of the geochemical environment can be achieved.

5.1.2.4.5 Planned Testing. The data obtained from testing described in this subsection will support the completion of Work Requirements W.2.4.A, W.2.5.A, W.2.5.B, W.2.7.B, W.2.8.B, W.2.9.B, W.2.10.B, W.2.15.B and W.2.17.B and the closure of Issues W.1.A and W.1.B.

5.1.2.4.5.1 Hydraulic Conductivity. The hydraulic conductivity of the waste package packing material is one of the key data requirements for waste package design and performance assessment. Packing material hydraulic conductivity determines the rate of mass flux and thus is the rate-controlling process for radionuclide release. If the hydraulic conductivity falls below a maximum value, then diffusion becomes the rate-controlling process relative to convection and the mass flux is minimized. Therefore, a sufficiently low hydraulic conductivity packing material will (1) minimize the mass flux of corrosive aqueous species to the waste container, (2) ensure sufficient residence time for the radionuclides in the packing materials to complete sorption/precipitation reactions, and (3) maintain diffusional control of radionuclide transport through the packing material. Hydraulic conductivity values are most influenced by the density, composition, and temperature of the packing materials. Consequently, a series of tests are being completed that measure hydraulic conductivity as a function of these parameters. These data will enable the waste package designer to specify packing materials density and composition that are required to ensure that the packing materials hydraulic conductivity falls below the maximum permissible value to maintain diffusional radionuclide transport.

A hydraulic conductivity test consists of placing a prepared sample in the column of the permeameter cell or the triaxial test system (Fig. 5-17 and 5-18) and applying a hydraulic head (pore pressure) to the sample. Radial and axial confining pressures are applied to the sample at the same time. A prepared test sample is a mixture of bentonite and crushed basalt (0.1 to 5 mm) compacted in a cylindrical mold to a density of 1.7 to 1.9 g/cm^3. The flow of the effluent that has passed through the sample is measured as a function of time. Using the Darcian flow equation, Q equals KiA, where Q equals the flow rate, i equals the hydraulic gradient, and A equals the area, the hydraulic conductivity (K) is calculated. Other test parameters can be varied for the test, including confining pressure and temperature.

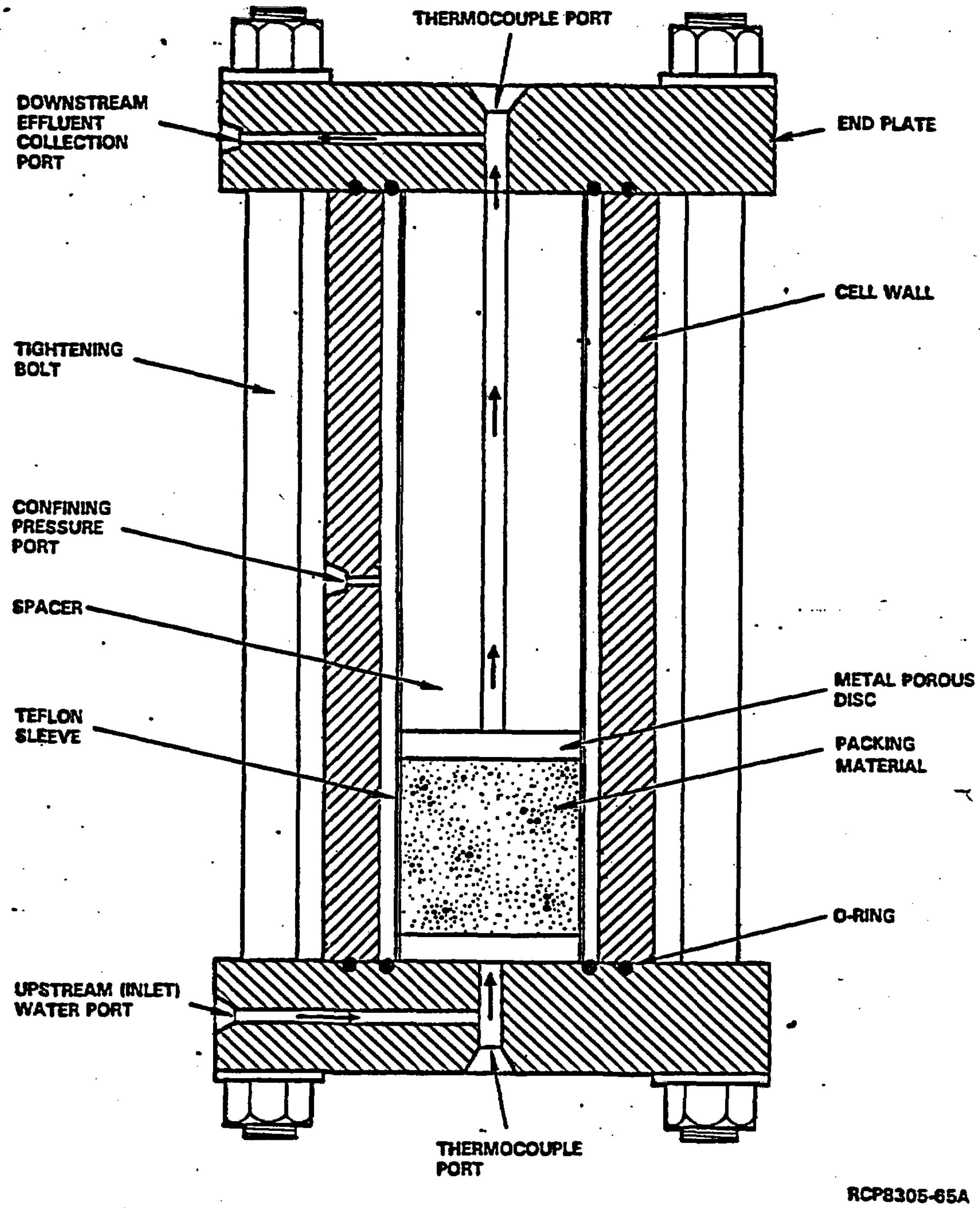


FIGURE 5-17. The Basalt Waste Isolation Project Permeameter Cell Cross Section for Measuring Hydraulic Conductivity.

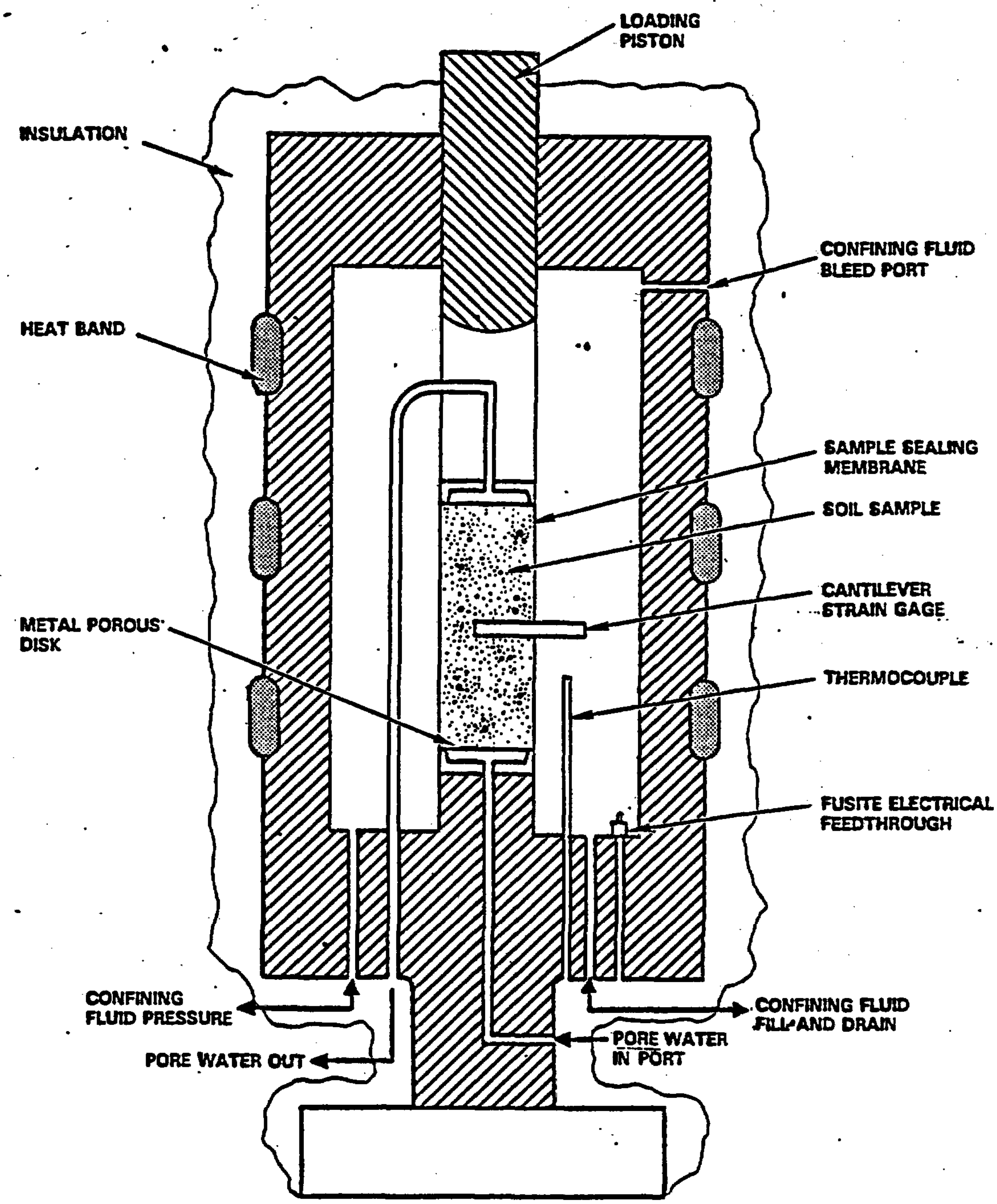


FIGURE 5-18. The Basalt Waste Isolation Project Triaxial Cell Cross Section for Measuring Hydraulic Conductivity.

Hydraulic conductivity testing in FY 1983 developed data for proposed bentonite/basalt compositions as a function of temperature and density. The range of packing materials densities and compositions for permeability and other physical testing in FY 1984 will be determined by evaluating results obtained from packing materials pneumatic emplacement testing conducted during FY 1983. The packing materials pneumatic emplacement demonstration test is being completed by the Westinghouse Waste Technology Services Division for the BWIP. Testing will be completed in FY 1984 to accurately determine hydraulic conductivity values as a function of temperature and density on a statistical basis. Also, hydraulic conductivity testing on bentonite/basalt mixes using bentonite dehydrated at 300°C will be performed in FY 1984. Emphasis in FY 1985 will be placed on hydraulic conductivity testing of hydrothermally altered packing material mixes in the triaxial and permeameter cells.

For design purposes, the hydraulic conductivity data will be used to specify packing materials composition and density at which an adequate hydraulic conductivity is achieved. For performance assessment, the data will be used along with radionuclide diffusion coefficients and retardation factors to predict radionuclide release from the packing material into the host rock.

5.1.2.4.5.2 Swelling Pressure. The swelling of the packing materials in a confined volume is a desirable property for the packing material component. Following emplacement, a period of dehydration is likely to occur in the packing materials, which may result in the formation of cracks. In addition, minor void spaces may exist in the packing materials that were left during the emplacement process. The presence of bentonite is expected to eliminate the possibility of significant void space in the packing materials because it increases in volume upon contact with water. In addition, bentonite will be sufficiently mobile to infiltrate a short distance into the larger fractures intersecting the borehole wall.

An acceptable range of swelling pressures will be recommended for the packing materials with an upper limit of the hydrostatic pressure (approximately 11 MPa). Hydrostatic pressure must not be exceeded so that the compressive strength of the container is not exceeded. Swelling pressure of the packing materials will be primarily a function of the packing materials density, bentonite content, and, to a lesser extent, temperature. Therefore, a series of tests are being run to determine the swelling pressure for basalt/bentonite mixtures over a range of different densities and temperatures.

A swelling pressure test is set up much like a hydraulic conductivity test. The packing materials sample containing bentonite is subjected to a hydraulic head and as it saturates it will swell, if unconfined. In the triaxial cell system, the swelling pressure is measured by recording the increase in confining pressure required to keep the sample volume constant in both the axial and lateral directions. When the confining pressure stops increasing, then saturation and the maximum swelling pressure have been achieved.

The objective of swelling pressure testing in FY 1984 is to obtain swelling pressure data for proposed bentonite/basalt compositions as a function of temperature and density. In particular, swelling pressure tests in FY 1984 will be completed on materials whose density and composition equals that emplaced by pneumatic methods in the packing materials emplacement test conducted in FY 1983. Swelling pressure tests will be initiated in FY 1984 with hydrothermally altered packing materials. Equipment modifications are under investigation to determine if swelling pressure tests can be conducted in the permeameter cells (see Fig. 5-17). Since swelling pressure and hydraulic conductivity data are generally taken from one sample, conversion of the permeameter cells would allow much more data to be acquired with minimal additional effort.

These data will enable the waste package designer to specify a packing materials composition and density that exhibits a swelling pressure that does not exceed hydrostatic pressure. These data have no impact on performance assessment except to ensure fracture healing that may have occurred during an early dehydration phase, thereby ensuring porous flow conditions and diffusional control of radionuclide transport.

5.1.2.4.5.3 Resaturation. During the early part of the containment period following emplacement of the packing materials and closure of the repository, high waste package temperatures (approximately 250°C) and low pressures (approximately 0.1 MPa) are expected to cause dehydration of the hydrated packing material, particularly sodium bentonite. With time, the packing materials temperatures will drop and pressures will rise such that groundwater will be stable as a liquid phase in the packing material. Subsequently, a wetting front will develop in the packing material and saturation will occur. Experimental determination of the temperatures at which saturation will occur is needed to predict the maximum temperature at which waste package hydrothermal interactions (e.g., container corrosion, waste form dissolution, and radionuclide sorption/precipitation reactions) can be expected to occur. The resaturation temperature is dependent on the vapor pressure that will exist in the packing materials as vapor moves through the packing materials. If vapor transport is sufficiently slow, vapor pressure will build up causing condensation and resaturation. Vapor transport rates will be affected by temperature and may be affected by packing materials composition, density, and length.

A resaturation test consists of placing a prepared sample in the column of the triaxial test system (see Fig. 5-18) and applying a hydraulic head (pore pressure) to the sample. The outlet end will be open to the atmosphere. Radial and axial confining pressures are applied to the sample at the same time. The flow of the effluent (vapor or liquid) that has passed through the sample is measured as a function of time. The hydraulic conductivity is calculated using the Darcian flow equation (see Section 5.1.2.4.5.1). If the vapor condenses to liquid during the experiment, a wetting front will be established and a swelling pressure will develop. Consequently, swelling pressure will be monitored during the experiment, and the moisture content of the sample will be analyzed as a function of distance from the water source following the experiment.

During FY 1984 scoping tests will be initiated to determine the temperature at which saturation will commence in the packing materials. If resaturation does occur at high temperatures in the scoping experiments, then the testing effort will be essentially complete. If resaturation does not occur at high temperatures, further bench-scale experiments will be designed (e.g., long column design) to determine the effect of packing materials length on vapor pressure buildup and condensation/resaturation in the packing materials. Such tests, if needed, will be designed and initiated in FY 1984 and completed in FY 1985. Full-scale waste package engineering tests will be conducted to determine whether or not the laboratory data are valid.

The resaturation temperature and time data will have little impact on waste package design. However, this information coupled with temperature versus time models of the packing materials will aid in the performance assessment of the waste package by (1) indicating the length of time a waste package will remain dry following repository closure and (2) indicating a maximum temperature at which waste package degradation processes (e.g., container corrosion and waste form dissolution) and radionuclide transport from the waste package to the host rock can occur. Because these processes are primarily dependent on temperature, a reduction in the hydrothermal temperature range will allow reduction in the uncertainty associated with the prediction of waste form dissolution, container corrosion, and radionuclide transport rates.

5.1.2.4.5.4 Shear Strength. The structural integrity of a packing materials mix is important in that the packing material must provide sufficient bearing strength to prevent subsidence of the container if the present horizontal emplacement concept is changed to vertical emplacement. Packing material shear strength will vary somewhat with particle size distribution. However, as long as basalt particle to particle contact is made, the packing materials should be structurally competent. Strength loss will occur, however, when too much clay is introduced into the packing materials mix, most likely at a ratio greater than 1:1 bentonite to basalt. The minimum required unconfined shear strength of a packing materials is approximately 0.896 MPa (130 lb/in^2) based on the current design weight of a loaded DHLW container (e.g., heaviest predicted waste package) with weight distributed evenly along the length of the container (AESD, 1983). Shear strength tests are conducted in the triaxial cell system on samples prepared in molds as described previously under hydraulic conductivity testing. The samples may be tested dry or saturated by applying an axial load on a confined or unconfined sample at a constant rate and recording sample deformation as a function of time until failure. In general, these tests may be conducted after completion of hydraulic conductivity and swelling pressure tests on the same samples. This approach is expected to save much time and effort in sample preparation.

Shear strength testing will be intiated in FY 1984 to determine the strengths of proposed bentonite/backfill compositions as a function of temperature, pressure, and density. If further testing is needed, it will be completed in FY 1985 on materials whose density and composition were defined by the Westinghouse Waste Technology Services Division packing materials pneumatic emplacement tests. For design purposes, these data will be used to refine the required basalt to bentonite ratio for the reference packing material.

5.1.2.4.5.5 Thermal Conductivity. An adequate thermal conductivity for the packing material is required to keep waste package temperatures below 300°C (AESD, 1983), since thermal conductivity values determine the rate at which heat dissipates from the container. Preliminary thermal conductivity testing of packing materials was initiated during FY 1983. The tests were conducted on 1:1, 1:3, and 3:1 mixes of dry bentonite/basalt at temperatures ranging from 60° to 250°C. Basalt particle sizes ranged from approximately 0.1 to 5 mm.

The thermal needle of line source method (Mitchell and Kao, 1978) was used to make thermal conductivity measurements. This method is based on the rate of temperature rise along a heat source within a homogeneous medium. A thermal needle, which contains a heat source and thermocouple, is embedded in a 10.2-cm-dia. sample. Heat is applied at a constant rate and the line temperature is measured as a function of time. The experimental results showed that density had the strongest effect on thermal conductivity values, basalt to bentonite ratios had a moderate effect, and particle size distribution and temperature had very little effect. Values of 0.50 ± 0.03 and 0.67 ± 0.03 were observed for mixtures of 75% crushed basalt/25% sodium bentonite at densities of 1.8 and 2.1 g/cm^3, respectively. The thermal conductivity values were insensitive to temperature.

The emphasis for thermal conductivity testing during FY 1984 will be placed on saturated mixes of materials of varying density and composition, including the density and composition of the materials emplaced by pneumatic methods in full-scale tests conducted at Westinghouse Waste Technology Services Division during FY 1983 and FY 1984. For design purposes, these data will be used to specify the packing materials composition and density that are characterized by adequate thermal conductivity to prevent unacceptably high peak temperature.

5.1.2.4.5.6 Radionuclide Transport (Test Description). Radionuclide transport in groundwater is usually described using the groundwater velocity field (predicted by hydrologic modeling techniques) and retardation factors (either predicted from sorption Kd and Kd isotherm data or measured in flowthrough column experiments) for reversible sorption reactions. The Kd is defined as the equilibrium or steady-state ratio of the amount of radionuclide sorbed on a gram of the solid to the amount of radionuclide left in a milliliter of solution. For very slow groundwater velocities, however, radionuclide transport will be dominated by diffusion rather than by convective groundwater flow. Therefore, two types of data are needed for describing the movement of each radionuclide in waste package backfill: (1) a retardation factor (R_f) and (2) an effective diffusion coefficient. The R_f can be related to the sorption Kd by the equation:

$$R_f = \frac{1 + \rho}{\theta} \times Kd \qquad (8)$$

where

ρ = to bulk density of packing material

θ = to porosity of packing material.

These data, along with hydraulic conductivity data and radionuclide solubility data, will be used to predict radionuclide release rates from the packing materials into the host rock. Tests to determine radionuclide solubilities in the packing materials under expected geochemical conditions are described in Section 5.1.2.2.4.2.

Three test techniques will be used to obtain radionuclide transport data for the packing material: (1) batch sorption/desorption tests, (2) flowthrough column tests, and (3) static diffusion cell tests. The solid and solution radionuclide concentrations from these experiments will be compared with similar data from static and flowthrough waste/barrier/rock interaction studies (see Section 5.1.2.1) to determine the effect of container degradation and waste form dissolution on radionuclide reactions in the packing materials.

Batch Sorption/Desorption Test. A batch sorption/desorption test is used to measure Kd values and sorption/desorption isotherms for radionuclides. The Kd or the sorption isotherms, packing material porosity, and packing material bulk density are then combined to calculate a retardation factor for a given radionuclide. Although these data are not directly applicable to a flowthrough situation, they provide a useful basis for estimating the relative capability of the basalt/bentonite mixture to retard radionuclide transport by sorption. The experimental data also provide estimates of time required to reach the steady-state or equilibrium distribution of radionuclides between solid and solution. Consequently, the influence of reaction kinetics in flowthrough experiments can be gaged by comparing radionuclide residence time in the flowthrough column with the time required to reach equilibrium conditions.

Measurement of a Kd value or a sorption isotherm using the batch test method consists of contacting a known volume of solution containing the radionuclide with a known amount of sorbing solid. The decrease in solution radionuclide concentration after reaching equilibration or steady-state conditions is then used to calculate the amount of radionuclide sorbed on the solid. The sorption isotherm describes how Kd varies as a function of radionuclide concentration.

For radionuclides having stable isotopes, chemical methods (inductively coupled plasma spectrometer, ion chromatograph, atomic absorption spectroscopy) are used to measure initial and final concentrations in solution if concentrations are high enough to be measured. Radioanalytical techniques must be used for these elements if their radioactive isotopes are used in testing instead of the stable isotopes. Similarly, for those radionuclides that have no stable isotopes, only radioanalytical techniques (X-ray or gamma-ray spectroscopy, surface barrier alpha spectroscopy, liquid scintillation, or gas flow proportional counters) can be used.

Important sorption test parameters include temperature, radionuclide oxidation state and concentration, competing and complex forming ion concentrations, the presence of organics, radiolysis, the clay to basalt ratio in the packing materials, and solid surface area. A significant amount of batch sorption testing has been completed at 60° and 150°C with key radionuclides (e.g., ^{139}I, ^{79}Se, ^{99}Tc, and the actinides) on crushed basalt and sodium bentonite (Ames and McGarrah, 1980; Salter et al., 1981a; Salter et al., 1981b; Ames, 1981). Batch sorption experiments initiated in FY 1983 will continue through FY 1985 at 90° and 150°C with bentonite/basalt mixtures. During this time, emphasis will be placed on achieving and monitoring Eh conditions in basalt/water systems experimentally without resorting to the use of an auxiliary reducing agent such as hydrazine.

<u>Static Diffusion Cell Tests</u>. Static diffusion tests will be used to determine the diffusion coefficients for radionuclides in the packing material. These coefficients are used to predict the radionuclide mass transport in the packing material when groundwater velocities are low enough to minimize advective transport. This technique requires the use of two open-ended short columns of packing materials placed end-to-end in contact inside a tight-fitting closed container. One column is initially tagged with a radionuclide such that, when the two columns are placed in contact, the initial concentration boundary conditions are those of a step function. The radionuclide is then allowed to diffuse from the tagged column into the untagged column for a known time period. The double column is sectioned and analyzed to determine the radionuclide distribution, and the diffusion coefficient is calculated from the diffusion time and the radionuclide distribution along the column.

Analytical techniques to be used in the diffusion cell tests will be the same as those used for determining the distribution of radionuclides sorbed on solids from the flowthrough column tests. The important variables in diffusion cell tests are temperature, bulk density, clay to basalt ratio of the packing materials, the effects of radiation, and initial radionuclide concentration.

During FY 1983, development of experimental equipment (i.e., a diffusion cell and a core slicing apparatus) was largely completed. In FY 1984, the diffusion cell will be designed, constructed, and tested for ease of sample preparation and water tightness, and slicing techniques will be developed. Also during FY 1984, diffusion cell tests will be initiated using radioactive tracers (e.g. ^{99}Tc, ^{238}U, ^{239}Pu, and ^{237}Np) and will be continued in FY 1985. Similar tests will be conducted with hydrothermally altered packing materials and in a radiation field commencing in FY 1985 and continuing into FY 1988.

<u>Flowthrough Column Tests</u>. The flowthrough column method can be used to measure an effective diffusion coefficient directly from which a R_f can be calculated. The R_f is then used to predict the migration velocity of that radionuclide relative to the groundwater velocity.

Two techniques can be used with the column method to measure R_f: (1) analysis of the effluent from the column for the radionuclide concentration or (2) direct measurement of the radionuclide sorbed on the solid in the column. For those radionuclides that are not highly sorbed (i.e., those with low Kd values), analysis of the effluent is most convenient. The effluent radionuclide concentration is monitored over time. When breakthrough of the radionuclide is observed, the total effluent volume collected (since the radionuclide was injected into the column) is noted. The R_f is calculated as the ratio of the effluent volume in which breakthrough was observed to the pore volume of the column (pore volume is the volume of the column times the porosity of the solids that fill the column).

Radionuclides that are strongly sorbed (higher Kd values) will require a long time to elute from the column. Under these conditions, it is more convenient to determine the distribution of radionuclides on the solid substrate. When this distribution is found, the distance the radionuclide has traveled inside the column is noted. The distance that water would travel in an infinitely long column of the same material is then calculated from the total effluent volume collected during the test, the column length and the pore volume. The R_f is the ratio of the distance traveled by the water to the distance traveled by the radionuclide.

There is additional data that can be obtained from the column tests. The shape of the radionuclide breakthrough curve or distribution of sorbed radionuclide is used to calculate the dispersion coefficient for that radionuclide. If groundwater velocities are sufficiently slow ($\leq 1^{-10}$ cm/s), the dispersion coefficient will be equal to the effective diffusion coefficient of that radionuclide.

Analytical techniques used to determine radionuclide concentrations in the effluent are the same as those used in the batch Kd measurement tests, except for the use of a large number of samples. Determination of the distribution of sorbed radionuclides in the column requires that (1) the column be sectioned into small samples and the radionuclide is stripped from the solid and analyzed (or analyzed without stripping if possible) or (2) nondestructive methods are developed to determine the radionuclide distribution. The variables that are studied in batch Kd measurements are also studied in flowthrough column tests (e.g., temperature, radionuclide oxidation state, and concentration). In addition, the bulk density of the solid, the groundwater flow rate, confining pressure, and pore water pressure will be varied in the flowthrough tests.

During FY 1984, work will concentrate on the development of experimental methodology to complete flowthrough experiments successfully with packing materials. Initial flowthrough experiments are being completed at room temperature with nonradioactive tracers to estimate the time required to complete experiments as a function of packing materials composition, density and extent of sorption. During FY 1984, off-the-shelf flowthrough systems to be used for radioactive testing will be evaluated and procured. Flowthrough tests will then commence in FY 1985 and continue through FY 1986 using radioactive tracers (e.g. ^{99}Tc, ^{238}U, ^{239}Pu, and ^{237}Np) at repository temperatures and pressures. Similar tests using hydrothermally altered packing materials will be initiated in FY 1987 and continue into FY 1990.

5.1.2.4.5.7 Hydrothermal Testing. The packing materials component of waste package is expected to function 10,000 yr or longer. This will require that the long-term stability of candidate materials be determined under conditions expected in a nuclear waste repository in basalt. This will be accomplished by hydrothermal testing under conditions (e.g., groundwater composition, temperature, pressure, and packing materials composition) relevant to a repository in basalt. The basic data acquired from these experiments are changes in solution concentration as a function of time, the time required to reach the steady-state solution condition, solution composition changes during the experiment, and analysis of the solids before and after the experiment. A comparison of the phase assemblages before and after hydrothermal reaction will indicate (1) the extent of initial packing materials phase alteration (i.e., the stability of the packing material), (2) the identification of the packing materials alteration products, and (3) the likely effect of hydrothermal alteration on key packing materials properties (e.g., thermal and hydraulic conductivity, groundwater buffering capacity, and sorptive capacity). These data, along with a study of natural mineral analogues of packing materials found in the host rock, will provide a reasonable estimate of potential packing material stability.

Hydrothermal experiments will be conducted at temperatures from 150° to 300°C and 30 MPa pressure (e.g., maximum temperatures and pressure). Synthetic Grande Ronde Basalt groundwater, which is representative of the composition of the field samples collected at the repository horizon and analyzed, will be used in the experiments.

Three types of experimental systems will be used, the Dickson-type rocking autoclave, the cold seal pressure vessel, and the Parr pressure vessel. The Dickson-type rocking autoclave allows sequential sampling of solution at temperature and pressure without perturbing the experimental system. A typical solution to solid ratio of 10:1 is used in the experiments to be conducted and experimental duration is typically 1 to 3 mo. However, longer term experiments (9 to 12 mo) are planned at lower temperatures ($\leq$150°C) to more accurately determine steady state solution compositions. These experiments are required because of the temperature-imposed constraints on chemical reactions (particularly formation of secondary minerals). The cold seal and Parr pressure vessel method consists of solids/solution mixed and placed in an inert capsule at a ratio of approximately 1:1. Experiment duration is typically 9 to 12 mo. During FY 1984, long-term low temperature (approximately 150°C) experiments of the packing materials/groundwater system will be initiated and will continue through FY 1990 followed by in-depth microcharacterization of solid run products.

5.1.2.4.6 Logic Network. The packing materials data required to support waste package design and performance assessment must be generated in a manner consistent with the design and performance assessment schedules. The relationship between the packing materials studies and input to the design and performance assessment efforts is shown in Figure 5-19.

5.1.3 Design and Development

5.1.3.1 Waste Package Design and Engineering Studies.

5.1.3.2 Waste Package Development Testing. (The above activity and subactivities will be included in the final draft of the Engineered Barriers Test Plan due September 30, 1984.)

5.1.4 Performance Evaluation

5.1.4.1 Near-Field Performance Evaluation.

5.1.4.2 Design Analysis.

5.1.4.3 Waste Package Field and In Situ Testing. (The above activity and subactivities will be included in the final draft of the Engineered Barrier Test Plan due September 30, 1984.)

5.2 TEST ENVIRONMENT

Barrier materials testing activities will be conducted both in laboratory and field environments. Laboratory tests will attempt to simulate, as closely as possible, the range of conditions expected in a nuclear waste repository in basalt. The need for field testing of engineering or full-scale waste packages arises when laboratory data are insufficient to verify design or performance models because important parameters, such as hydrologic conditions, geochemical properties, in situ stresses, or mining effects, cannot be completely reproduced in the laboratory.

Several basalt flows in the Grande Ronde Basalt Formation are being considered as possible repository horizons because they are at a depth sufficient to isolate the waste from effects of upper aquifers and erosion, and they have sufficient thickness and lateral extension. These flows include the Umtanum, McCoy Canyon, Rocky Coulee, and Cohassett flows. Testing will continue using the Cohassett flow reference basalt. The ranges of variables (Eh, pH, and groundwater compositions) to be used in barrier

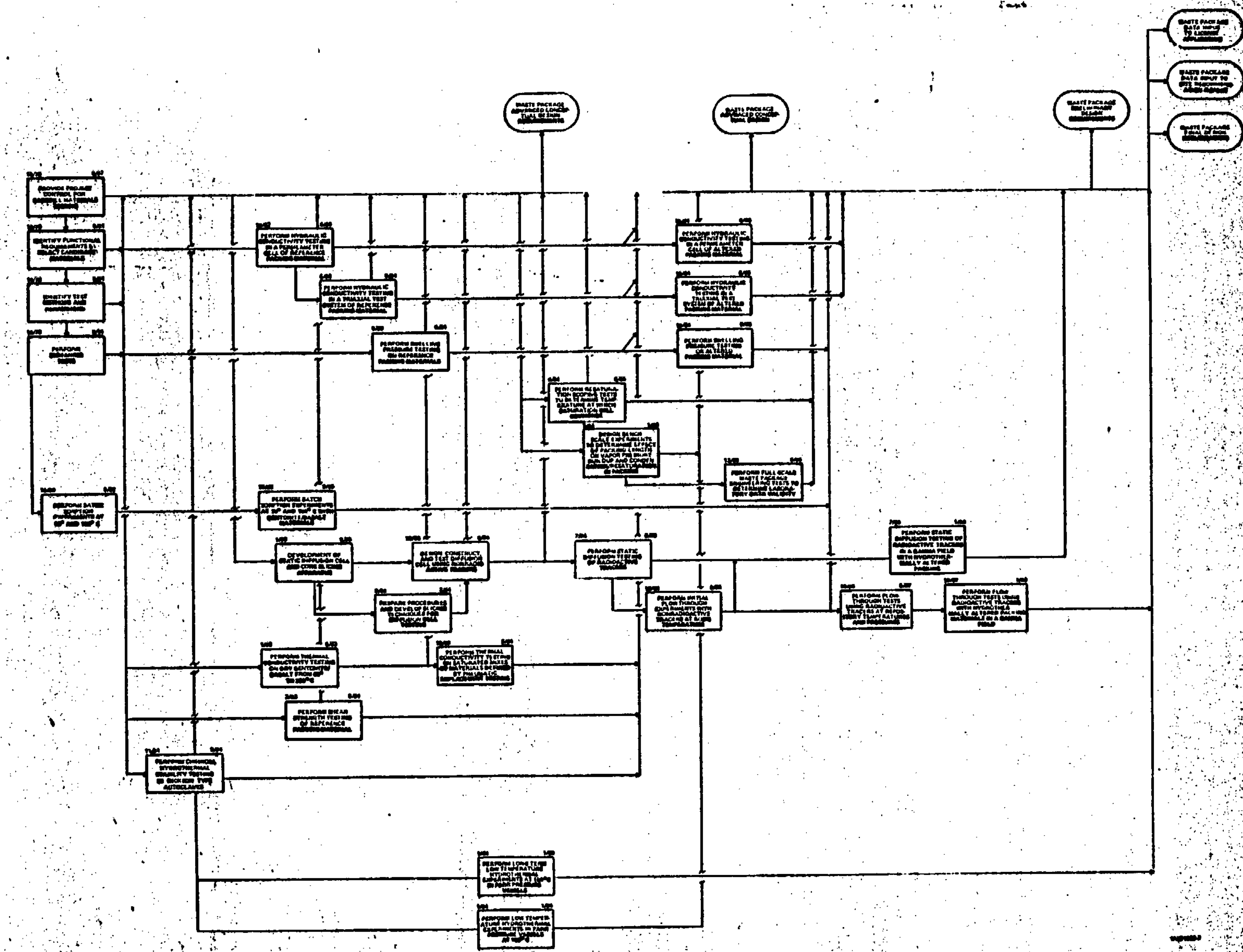


FIGURE 5-19. Packing Materials Testing Logic Diagram.

materials laboratory testing will cover those expected in the environment of this flow. The geologic materials involved include, in addition to the basalt from this flow (taken from various levels in the flow-entablature, colonnade, and flow top), interbed materials and associated groundwater. The geologic solids and groundwater will be thoroughly characterized in the laboratory before field testing begins to define the environment of the tests. Solid characterization will include the following:

- Chemical and mineral composition
- Porosity and density
- Surface area and particle size
- Ion exchange capacity.

Groundwater characterization will include:

- Chemical composition
- Eh
- pH.

The variables that are expected to effect the results of barrier materials testing and are controlled by the repository environment are temperature; pressure; groundwater composition, pH, and Eh; radionuclide identity and concentration; groundwater flow rates; basalt and interbed composition; and barrier materials composition. The ranges of values for these variables to be used in the tests will be determined by the best information available on the repository environment at the time tests are begun. Characterization of the repository environment is continually evolving through computer modeling and measurement.

5.3 RESOURCES AND FACILITIES

The equipment required for specific barrier materials laboratory and field tests is described in Section 5.1. In addition to this equipment, laboratory and support facilities will be required. Laboratory facilities are required for the set up and performance of the tests and for analyses of proposed barrier materials, geologic solids, and groundwater solutions both before and after testing. A wide variety of analyses will be required for supporting the tests: radiochemistry, groundwater analysis (including Eh, pH, cation, and anion concentrations), solid and surface analysis (X-ray diffraction, chemical analysis, scanning transmission electron microscope, scanning electron microscope, microprobe analysis), and others. The laboratories currently available for performing the tests and analytical work include: the Basalt Materials Research Laboratory in 2101-M, 200 East Area (nonradioactive waste forms tests and groundwater, solid, and surface analysis); the 222-S Laboratory, 200 West Area (tracer-loaded and fully radioactive waste form hydrothermal testing and radiochemistry); the 325 Building, 300 Area (tracer-loaded and fully radioactive waste form hydrothermal testing and radiochemistry); and the 326 Building, 300 Area (nonradioactive solids characterization).

5.4 DATA

The test data to be developed by the barrier materials test program are specified in detail in Section 5.1 for each activity (Waste Form, Barriers Materials, Design and Development, and Performance Evaluation). These data will be delivered in one of the following forms:

- Data records of observations, tests, measurements, and specimen sources
- Objective evidence such as photographs, strip charts, data tapes, etc.
- Materials specimens resulting from testing.

5.4.1 Data Recording and Storage

Procedures for data and sample control have been implemented in each of the BWIP laboratories and BWIP contractor laboratories responsible for barrier materials testing. Procedures used by BWIP contractors are reviewed and approved by Rockwell to assure consistency with Rockwell procedures. These procedures provide requirements for traceability of data and reports issued by the laboratories (sample identification, control, archiving, and data recording). These procedures must be in compliance with the national concensus standard (ANSI/ASME, 1983). Applicable procedures given in the BWIP operating procedures manual (Rockwell, 1983b) are as follows:

C-4.3.1 - Sample Control System for BWIP Materials Control Laboratory

C-4.3.2 - Data and Sample Control System for Basalt Solution Chemistry Laboratory

C-4.3.3 - Data and Sample Control System for Basalt Solids Characterization

C-4.3.4 - Data Specimen Traceability for Rock Mechanics Laboratory

C-4.3.5 - Data and Sample Control System for BWIP Hydrothermal Laboratory

C-4.3.6 - Data and Sample Control System for BWIP Metallurgical Testing Laboratory

C-4.3.7 - Data and Sample Control System for Backfill Materials Testing.

Documentation produced by the Engineered Barriers Department and its contractors must be traceable to the original laboratory data. All steps in analysis of the data must also be documented to preserve the traceability of data. The data and analyses can be written as a supporting document and entered into the BWIP Engineering Release System (Rockwell, 1982b, Procedure 5-6; Rockwell, 1983b, Procedure E-5). The data and analyses will be entered into the BWIP Records Management System for archiving, specifically to support licensing.

The primary record keeping system for the BWIP is the bound, numbered, laboratory data notebook. (Entries in controlled notebooks are specified in Rockwell, 1983b, Procedure E-9.) This is a Rockwell-issued, controlled document with an assigned number and consecutively numbered pages. Each experiment will be recorded in experimental laboratory data notebooks dedicated to a defined series of experiments. To ensure the reproducibility and traceability of experiments, all experimental conditions, procedures, and results will be recorded in detail. All samples and materials used in (or produced by) the experiment will be assigned unique identification numbers with appropriate labels for identification and traceability.

Other types of records include requests for analyses, analytical reports, archive logs, sample number logs, and experimental reports. The first two types of records are forms that are used to assist in providing the traceable link between analysis requestors and analysis laboratories. The logs refer to specific samples analyzed or used in experiments. The numbers assigned to these samples become a reference for all subsequent analysis and characterization by other laboratories. An experimental report is a formal Rockwell document prepared in accordance with the Rockwell technical information manual (Rockwell, 1984). This controlled document will be used by the experimenters to report interpretations and conclusions about experiments and data. The document will be distributed to users and to archives for permanent record.

5.4.2 Data Analysis

The data obtained from the tests described in this plan will be used to evaluate candidate waste package materials for designs and provide data for development of waste package performance assessment models. These data will ultimately support the licensing of the repository through the use of the performance assessment models and reliability testing of waste packages. Because of requirements by licensing , the data must be defensible and their reliability, traceability, applicability, and completeness must be known. Careful experimental design will assure that the data are applicable to test plan objectives and that all significant experimental variables have been considered. The use of statistical experimental designs will be employed where appropriate for obtaining required data. As discussed in Appendix A, it is necessary to plan the experiments with statistical analysis in mind if maximum information is to be obtained from a given amount of experimental work. Statistical designs will also be required to extrapolate short-term materials behavior obtained under accelerated conditions to long-term behavior for which models must be used to predict performance.

Statistical analysis of the experimental data will be performed to determine the reproducibility and accuracy of the data. Estimation of random errors, that lower the reproducibility, will be obtained by making a sufficient number of observations. Standard statistical methods will be used to estimate the probable error.

Analysis of the data will often require the determination of a quantitative relationship between two (or more) variable quantities. Linear and nonlinear regression analysis will be performed on the data to obtain this relationship. Regression coefficients will be calculated and the precision of the regression equation will be estimated by standard statistical techniques. It should be noted that the nature of the derived regression equation requires that it be interpreted with caution since the expression is valid only for the range of the variables measured.

5.4.3 Instruments and Equipment

The types of instruments and equipment required by the barrier materials testing program are identified and described in Section 5.1 for each test. Established BWIP procedures that govern testing and data acquisition set forth sensitivity (i.e., measurement accuracy), calibration, and other requirements for test instruments and equipment. The procedures also identify statistical errors that may be introduced into test results from instruments and equipment.

6.0 TEST PROCEDURES AND INSTRUCTIONS

All testing activities defined in Section 5.1 of this test plan shall be performed in accordance with Rockwell procedures as they are now or will be defined in RHO-BWI-MA-4. Procedures governing the acquisition, recording, and storage of data to be used in the NRC licensing process shall be qualified in accordance with ANSI/ASME (1983). Procedures that are currently authorized are listed below.

Established

C-4.3 Test Specimen (Sample) Control System for the BMRL
C-4.3.1 Data and Sample Control for Solution Chemistry Laboratory
C-4.3.2 Data and Sample Control for Basalt Solids Characterization
C-4.3.3 Data and Specimen Traceability for Rock Mechanics Laboratory
C-4.3.4 Data and Sample Control System for Hydrothermal Laboratory
C-4.3.5 Data and Sample Control System for Metallurgical Testing
C-4.3.6 Data and Sample Control System for Backfill Materials Testing
C-4.3.7 Data and Sample Control System for the Concrete and Grout Laboratory
C-4.5 On-the-Job Training for Hydrothermal Equipment
C-4.6 Dickson Rocking Autoclaves
C-4.7 222-S Tracer Laboratory Dickson Rocking Autoclave
C-4.8 LECO Cold Seal Autoclave
C-4.9 Barnes Rocking Autoclave
C-4.10 Radiation Safety, Training, and Operating Requirements for BMRL X-ray Diffraction Laboratory
Appendices:
A X-ray Exposure Emergency Instructions
B Qualified Operators, BMRL X-ray Diffraction Laboratory
C-4.11 X-ray Diffraction (General)
C-4.12 Electron Microprobe (EMP) Analyses
C-4.13 Scanning Transmission Electron Microscope (STEM)
C-4.14 Scanning Electron Microscopy (SEM)
Appendix:
A Preparation and Examination of Radioactive Samples, Scanning Electron Microscope (SEM)
C-4.15 Preparation of Standard Sieve Basalt From Basalt Monoliths
C-4.16 Preparation of Basalt for Hydrothermal Testing
C-4.17 COR-2 Potentiodynamic Corrosion Measurements Using the PAR 350A Corrosion System
C-4.18 COR-1 Electrochemical Corrosion Sample Preparation
C-4.19 LADD Research Industries Carbon Coater
C-4.20 Unassigned
C-4.21 Sample Preparation, Metallographic and Petrographic Examination
C-4.22 Swell Pressure Hydraulic Conductivity and Strength Tests for Soils Using the Triaxial Cell System
C-4.23 Hydraulic Conductivity of Soil Samples

C-2.4 Groundwater Sampling and Analysis

Appendices:

- A General Field Collection Method for Groundwater Samples
- B Sampling Method for Major Cations and Trace Elements in Groundwater
- C Field Measurement of Total Alkalinity
- D Field Measurement of Groundwater Temperature
- E Measurement of Groundwater pH
- F Measurement of Specific Electrical Conductivity in Groundwater
- G Well Sampling Method for Oxygen Isotope Ratio and Hydrogen Isotopes Ratio
- H Well Sampling Method for $^{13}C/^{12}C$ $^{34}C/^{32}S$ Isotopic Ratios and Carbon-14
- I Well Sampling Methods for $^{34}S/^{32}S$ Isotopic Ratios
- J Well Sampling Method for Dissolved Gases
- K Analysis of Major, Minor, and Trace Cations in Solutions by Inductively Coupled Plasma (ICP) Spectrometer
- L Well Sampling Method for Uranium
- M Well Sampling Method for Low Level Tritium
- N Field Measurement of Oxidation-Reduction Potential in Groundwater
- O Laboratory Measurement of Total Alkalinity
- P Field Collection Method for Argon-Lifted Groundwater Samples
- Q Well Sampling Method for ^{36}Cl
- R Field Measurement of Groundwater Turbidity
- S Analysis of Ions in Aqueous Solution Using Ion Chromatography
- T Colorimetric Measurement of Thiocyanate in Groundwater
- U Analysis of Total Carbon and Total Organic Carbon in Aqueous Solution
- V Measurement of Trace Elements in Aqueous Solutions By Graphite Furnace Atomic Absorption Spectroscopy
- W Sampling of Precipitation for Oxygen and Hydrogen Isotopic Ration
- X Sampling of Fluorescein Dye from Groundwater during Borehole Development

7.0 SAFETY

All operations required to complete the work detailed in the BMTP will be carried out in accordance with Rockwell safety procedures. These include, but are not limited to, the following:

RHO-MA-139	Environmental Protection Manual
RHO-MA-145	Radiation Monitoring Manual of Standard Practices
RHO-MA-172	Radiation Work Procedure
RHO-MA-220	Rev 1, Radiological Standards and Operational Controls
RHO-MA-221	Accident Prevention Standards (2 volumes)
RHO-MA-278	ALARA Program.

Each new facility or equipment installation will have its design plans and/or safety assessment document reviewed and approved by the Rockwell Health, Safety, and Environment Function. Each testing task will have a detailed, step-by-step procedure which will be approved by the Radiological Engineering Group for the Health, Safety, and Environment Function. These procedures will be readily available to the workers involved in the task. In many cases the facility in which the test is to be performed will have procedures covering the safety aspects of the test. Where this is not the case, the BWIP procedures need not repeat the details, but may merely refer to the relevant safety procedures. Any differences between the specific procedure and the general facility procedure will, however, be fully developed. Procedure departure authorizations will be obtained for any situation where it is felt that the in-place procedures are inadequate and time does not permit a revision.

All new equipment or processes used to perform barrier materials testing will be described in safety procedures and forwarded to a relevant safety review committee within the Health, Safety, and Environment Function for approval.

7.1 CONTRACTOR REQUIREMENTS

Non-Rockwell contractors associated with the BWIP barrier materials testing will be responsible for safety considerations and procedures in those portions of the project over which they have control.

8.0 ENVIRONMENTAL EFFECTS

The majority of the materials evaluation studies defined in the BMTP will be conducted in laboratory or hot cell facilities. No adverse environmental effect is expected to result from the tests.

9.0 QUALITY ASSURANCE

9.1 INTRODUCTION

Rockwell maintains an effective quality assurance program (Nicol, 1983) in accordance with DOE-RL Order 5700.1a (DOE-RL, 1983), to assure the requisite level of quality is maintained throughout all areas of the BWIP.

This quality assurance program plan establishes the minimum activities applicable to the engineered barrier material testing program (Nicol, 1983, Table 1). These activities are defined in national concensus standard ANSI/ASME NQA-1 (1983), and are applicable to all project participants.

9.2 REQUIREMENTS

To assure uniformity in execution of the quality assurance program by Rockwell and on projects under technical direction of Rockwell, the following BWIP-specific requirements are established in addition to the basic and supplemental quality assurance criteria of ANSI/ASME NQA-1 (1983).

9.2.1 Organization

Interfaces, functional responsibilities, levels of authority, and lines of communication between Rockwell and other project participants will be established in the Engineered Barrier Materials Project Management Plan. The project management plan is designed to ensure the organizational structure provides for verification of quality achievement by persons or organizations not directly responsible for performing the work.

9.2.2 Quality Assurance Program

All organizations providing goods or services in support of engineered barrier materials testing are required to implement a quality assurance program in accordance with requirements herein, encompassing the scope of activities defined in their respective contracts. Quality assurance programs of suppliers are submitted to Rockwell for review and approval prior to commencement of work.

9.2.3 Design Control

Engineering and experimental design activities, required as a result of testing activities defined in this plan, are controlled in accordance with BWIP configuration management requirements set forth in Rockwell (1983c) to ensure strict adherence to technical baseline criteria presented in the BMTP. Responsibilities and authorities for design activities performed by subcontractors and suppliers are defined in formal written statements of work, plans, and contract documents.

9.2.4 Procurement Document Control

Procurement documents are to incorporate requirements contained herein. Rockwell Quality Assurance is responsible to review and approve procurement documents generated by Rockwell to ensure their adequacy and content prior to placement of contracts. Procurement documents processed by BWIP suppliers are subject to review and approval by the suppliers' quality assurance organizations, and are subject to surveillance and audit by Rockwell Quality Assurance.

9.2.5 Instructions, Procedures, and Drawings

Documentation that is produced by other contractors in support of BWIP barrier materials testing and that is used to define or control work requires advance approval by the BWIP. Schedules for submittals and designated approval authorities are provided in statements of work and contract documentation.

9.2.6 Document Control

Documentation described in Section 9.2.5 is to be controlled in accordance with the suppliers' Rockwell-approved document control procedures. The supplier is responsible to ensure documentation is prepared, reviewed, and approved by qualified technical personnel, and is traceable both to criteria and records. Barrier materials testing end-item documentation is issued through the Rockwell document control system.

9.2.7 Control of Purchased Items and Services

Rockwell Quality Assurance is responsible to ensure goods and services procured for the BWIP conform to procurement documents. This is accomplished through procurement document review, source surveys, supplier surveillances, receiving inspections, and audits.

Application of quality assurance requirements by BWIP suppliers to subtier suppliers is the responsibility of the BWIP suppliers. This activity, however, is subject to surveillance and audit by Rockwell Quality Assurance. This requirement also applies to suppliers contracted by other DOE-RL contractors providing goods and services to the BWIP.

9.2.8 Control of Measuring and Test Equipment

Each DOE-RL contractor and supplier is to submit procedures for control of measuring and test equipment to the BWIP for approval. This includes, but is not limited to, methods for calibration which are traceable to National Bureau of Standards or other nationally recognized standards, and requirements for controlling use of equipment, including recall for items past calibration due dates. Test data are to be traceable to appropriate standards and subject to the supplier's internal review prior to final approval.

9.2.9 Control of Nonconforming Items

Items that do not conform to specified requirements are to be withheld from use pending receipt of written disposition by Rockwell via a Nonconformance Report or a Supplier Disposition Request, as established in the statement of work.

9.2.10 Corrective Action

In addition to the suppliers' internal corrective action systems, Rockwell Quality Assurance is authorized to initiate formal request for corrective action to any participant when circumstance warrants. Each supplier is to be responsive to such requests in accordance with instructions provided as part of the Corrective Action Request form.

9.2.11 Quality Assurance Records

The BWIP conducts a records management system in accordance with ANSI/ASME NQA-1 (1983) and approved internal plans and procedures. Documentation required of suppliers is to be clearly identified in each respective statement of work to ensure BWIP records retention goals are met. These specific requirements are found in Rockwell (1983b, Section E-6).

9.2.12 Audits

Rockwell assumes overall audit responsibility for the barrier materials testing program. Rockwell audits are performed in addition to internal supplier audits as may be required as part of a suppliers' quality assurance program. A 10-day written notice proceeds formal Rockwell audits.

In addition to formal audits, Rockwell Quality Assurance maintains an aggressive surveillance program. Suppliers are to be responsive to Rockwell surveillance reports. Surveillances are generally conducted following a 4-day prior notice. Supplier surveillances are conducted in the presence of a supplier representative, when practicable.

12.3 MONTHLY TEST REPORTS

12.3.1 Contractor Reports

The team leader will furnish the Engineered Barriers Department Manager with two copies of a monthly report clearly showing, for each statement of work, the status of work accomplished, problems and solutions, and schedule and cost. Cost reports will be keyed to each statement of work, except in those cases where reporting by task(s) has been agreed upon by the participants.

12.3.2 Report Content

Monthly technical progress during the reporting period will be briefly presented in the following format for each statement of work:

- Work accomplished during the reporting month
- Problem areas and recommended solutions
- Schedule status and planned work for the next two months including
  - Percentage of work completed for each milestone
  - Estimated completion dates
- Expenditures, including
  - Prior month and cumulative actual cost
  - Current month estimated cost
  - Estimated remaining cost for current fiscal year.

12.4 INPUT TO BASALT WASTE ISOLATION PROJECT MONTHLY REPORTS

The Engineered Barriers Department Manager will use the information from contractor team leaders and internal BWIP weekly briefing reports to prepare the BWIP monthly report. Information to be presented includes:

- Major accomplishments since last report
- Significant problems and solutions. Note that previously reported problems will continue to be reported until a final solution is reported
- Summary of cost and schedule performance. Any developments or pending developments which may impact project estimates and/or schedules will be discussed
- Milestone schedule and report.

12.5 MEETINGS

12.5.1 Project Status Review Meetings

Contractor review meetings will be conducted periodically as required by statements of work. These meetings will include participation by BWIP and contractor personnel. Written notification of the meetings will be issued one week in advance of the meeting date. The meetings will be oriented towards resolving any potential problem areas. Current status and specific areas of concern will be discussed and near-term future activities identified. Meeting minutes will be issued following the meeting and will include any action items assigned. The test status review meeting will be used to present information contained in the monthly reports submitted by the team leaders and Rockwell BWIP personnel. The meeting will be held prior to submittal of the Waste Package End Function monthly report so that significant results from the meeting can be incorporated into the report.

12.5.2 Other Project Meetings

Other test program meetings may be called just prior to the start of the test program and may continue through the life of the program as needed. Meetings will be called at the discretion of the contractor team leader, his delegate, or by the Engineered Barriers Department Manager. Participation will be determined by the topics to be discussed.

13.0 REFERENCES

AESD (1983), "Waste Package Backfilling Process Development Test Plan," AESD-TME-3169, Westinghouse-Advanced Energy Systems Division for Rockwell Hanford Operations, Richland, Washington.

Allen, C. C. and M. B. Strope, Microcharacterization of Basalt--Considerations for a Nuclear Waste Repository, RHO-BW-SA-294 P, Rockwell Hanford Operations, Richland, Washington.

Altenhofen, M. K. (1981), 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.

American Public Health Association (1976), American Water Association, Water Pollution - Control Federation, "Standards, Methods for the Examination of Water and Wastewater," 14th Edition, p. 440-454.

ASME/ANSI (1983), Quality Assurance Program Requirements for Nuclear Facilities, NQA-1, American National Standards Institute/American Society of Mechanical Engineers, New York, New York.

ASTM (1976), Annual Book of ASTM Standards, Part 31, 1976, D 888-66 (Reapproved 1971), "Standard Methods of Test for Dissolved Oxygen in Water," p. 378.

Ames, L. L. (1981), Basalt Radionuclide Reactions: Fiscal Year 1981 Annual Report, PNL-3992, Pacific Northwest Laboratory, and RHO-BW-CR-127 P, Rockwell Hanford Operations, Richland, Washington.

Ames, L. L. and J. E. McGarrah (1980), Basalt Radionuclide Distribution Coefficient Determinations FY 1979 Annual Report, PNL-3146, Pacific Northwest Laboratory, Richland, Washington.

Ames, L. L. and J. E. McGarrah (1981), Investigation of Basalt-Radionuclide Distribution Coefficients: Fiscal Year 1980 Annual Report, RHO-BWI-C-108/PNL-3462, Pacific Northwest Laboratory for Rockwell Hanford Operations, Richland, Washington.

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

Anantatmula, R. P. et. al. (1983), Corrosion Behavior of Low Carbon Steels in Grande Ronde Groundwater in the Presence of Basalt-Bentonite Backfill, RHO-BW-SA-314 P, to be published in proceedings of Materials Research Society Mtg., November 14-17, 1983, Boston, Massachusetts, 12 p.

Anderson, W. J. (1982), Conceptual Design Requirements for Spent Fuel, High-Level Waste, and Transuranic Waste Packages, RHO-BW-ST-25 P, Rockwell Hanford Operations, Richland, Washington.

Apps, J. A., C. L. Carnahan, P. C. Lichtner, M. C. Michel, D. Perry, R. J. Silva, O. Weres, and A. F. White (1983), Status of Geochemical Problems Relating to the Burial of High-Level Radioactive Waste, 1982, NUREG/CR-3062/LBL-15103, Lawrence Berkeley Laboratory, University of California, Berkeley, California.

Apted, M. J. (1982), Overview of Hydrothermal Testing of Waste Package Barrier Materials at the Basalt Waste Isolation Project, RHO-BW-SA-228 P, Rockwell Hanford Operations, Richland, Washington.

Apted, M. J. and P. E. Long, Geochemical Characterization of Basalt/Groundwater Interaction for a Nuclear Waste Repository at the Hanford Site, Washington, RHQ-BW-SA-215A P, Rockwell Hanford Operations, Richland, Washington.

Apted, M. J. and J. Myers (1982), 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.

Arnett, R. C., R. D. Mudd, R. G. Baca, M. D. Martin, W. R. Norton, and D. B. McLaughlin (1981), Pasco Basin Hydrologic Modeling and Far-Field Radionuclide Migration Potential, RHO-BWI-LD-44, Rockwell Hanford Operations, Richland, Washington.

Barney, G. S. (1982), FY 1981 Annual Report - Radionuclide Sorption on Basalt Interbed Materials, RHO-BW-ST-35 P, Rockwell Hanford Operations, Richland, Washington.

Barney, G. S. (1981), Radioactive Reactions with Groundwater and Basalts from Columbia River Basalt Formations, RHO-SA-217, Rockwell Hanford Operations, Richland, Washington.

Berry, W. E. (1982), "Corrosion by Water and Steam: NACE Basic Corrosion," National Association of Corrosion Engineers, p. 7-8, 7-9.

Bradley, D. J., D. G. Coles, F. N. Hodges, G. L. McVay, and R. E. Westerman (1983), Nuclear Waste Package Materials Testing Report: Basaltic and Tuffaceous Environments, PNL-4452, Pacific Northwest Laboratory, Richland, Washington.

Chambre, P. L., T. H. Pigford, and S. Zavosky (1982), Solubility-Limited Dissolution Rate in Groundwater, ULB-NE-4016, University of California at Berkeley, Berkeley, California.

Charles, R. W. and G. K. Bayhurst (1983), "Rock-Fluid Interactions in a Temperature Gradient: Biotite Granodiorite + H_2O," J. of Volcan. Geoth. Res., 15, p 137-166.

Cherry, J. A., A. U. Shaikh, D. E. Tallman, and R. V. Nicholson (1979), "Arsenic Species as an Indicator of Redox Conditions in Groundwater," In W. Back and D. A. Stephenson (Guest Editors) Contemporary Hydrogeology - The George Burke Maxey Memorial, Vol. J. Hydrology, 43: p. 373-392.

Cleveland, J. M., T. F. Rees, and K. L. Nash (1983), "Plutonium Speciation in Selected Basalt, Granite, Shale, and Tuff Groundwater," Nuclear Technology, Vol. 62, p. 298-310.

Coles, D. G. and F. Bazan (1982), "Continuous-Flow Leaching Studies of Crushed and Cored SYNROC,: Nuclear Technology 56, p. 226-237.

Danielson, M. J., O. H. Koski, and J. Myers (1983), Development of High Temperature and Pressure Eh and pH Sensing Instruments," RHO-BW-SA-322 P, Rockwell Hanford Operations, Richland, Washington.

Dibble, W. E. and J. M. Potter (1982), Effect of Fluid Flow Rates on Geochemical Processes, SPE-10994, Society of Petroleum Engineers of AIME, Dallas, Texas.

Dibble, W. E. and W. A. Tiller (1981), "Non-Equilibrium Water/Rock Interactions. I. Model for Interface-Controlled Reaction," Geochim. Cosmochim. Acta, 45, p. 79-92.

DOE-RL (1983), Quality Assurance, DOE-RL Order 5700.1a, U.S. Department of Energy-Richland Operations Office, Richland, Washington.

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

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

EPA (1979), Methods for Chemical Analysis of Water and Wastes, Environmental Monitoring and Support Lab, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

EPA (1982), "Environmental Protection Agency, 40 CFR Part 191, Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes," Federal Register, Vol. 47, No. 250, U.S. Environmental Protection Agency, Washington, D.C.

Fish, R. L. and R. P. Anantatmula (1984), Preliminary Corrosion Models for BWIP Canister Materials, SD-BWI-TI-159, Rockwell Hanford Operations, Richland, Washington.

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

Gray, W. J. (1983), Gamma Radiolysis Effects on Grande Ronde Basalt Groundwater, RHO-BW-SA-315 P, Rockwell Hanford Operations, Richland, Washington.

Gilbert, I. W., T. D. Behymer, and H. B. Castaneda (1982), "Determination of Dissolved Oxygen in Natural and Waste Water," American Laboratory, 14(3).

Howard, J. and W. White (1981), "Clay Metamorphism: A Natural Analog for Argillaceous Backfill Behavior," in Proceedings of the 1981 National Waste Terminal Storage Program Information Meeting, U.S. Department of Energy, Columbus, Ohio.

Jantzen, C. M. (1983), Methods of Simulating Low Radox Potential for a Basalt Repository, DP-MS-83-59X, Savannah River Laboratory, E. I. duPont de Nemours and Company, Aiken, South Carolina.

Jacobs, G. K. and M. J. Apted, Eh and pH Conditions for Groundwater at the Hanford Site, Washington: Implications for Radionuclide Solubility in a Nuclear Waste Repository Located in Basalt, RHO-BWI-SA-174, Rockwell Hanford Operations, Richland, Washington.

Keith, T. E. C., D. E. White, and M. H. Beeson (1978), Hydrothermal Alteration and Self-Sealing in Y-7 and Y-8 Drill Holes in Northern Part of Upper Geyser Basin, Yellowstone National Park, Wyoming, U.S. Geological Survey Prof. 1054A.

Lane, D. L., T. E. Jones, and M. H. West (1983), Preliminary Assessment of Oxygen Consumption and Redox Conditions in a Nuclear Waste Respoitory in Basalt, RHO-BW-SA-283, Rockwell Hanford Operations, Richland, Washington.

LANL (1982), Summary Report on the Geochemistry of Yucca Mountain and Environs, LA-9328-MS, Los Alamos National Laboratory, Los Alamos, New Mexico.

LaQue, F. L. and H. R. Copson (1965), Corrosion Resistance of Metals and Alloys, Reinhold Publishing Corporation.

Long, P. E., R. D. Landon, R. W. Cross, K. R. Fairchild, and M. A. Chamness (1983), Geology and Petrology of Candidate Repository Horizons in Long, P. E. (editor) Repository Identification Report, Vol. 1; Comparative Evaluation of Candidate Repository Horizons Within the Reference Repository Location, RHO-BW-ST-28 P, Rockwell Hanford Operations, Richland, Washington.

McVay, G. L. and C. O. Buckwalter (1983), "Effect of Iron on Waste-Glass Leaching," J. Am. Ceramic Society, 66.

Mitchell, J. K. and T. C. Kao (1978), "The Measurement of Soil Thermal Resistivity," Journal of the Geotechnical Engineering Division ASCE, 104.

Moore, D. E., C. A. Morrow, and J. D. Byerlee (1983), "Chemical Reactions Accompanying Fluid Flow Through Granite Held in a Temperature Gradient," Geochemical et Cosmochimica Acta, 47.

Myers, J., M. J. Apted, and J. J. Mazer (1983), 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.

Nicol, M. F. (1983), Quality Assurance Program Plan, RHO-QA-PL-3, Rockwell Hanford Operations, Richland, Washington.

Niedrach, L. (1980), "Oxygen Ion Conducting Ceramics: A New Application in High Temperature-High Pressure pH Sensors," Science, 207.

NRC (1983a), Nuclear Regulatory Commission, 10 CFR Part 60, Disposal of High-Level Radioactive Wastes in Geologic Repositories, Technical Criteria, Federal Register, 48 (120), U.S. Nuclear Regulatory Commission, Washington, D.C.

NRC (1983b), Draft Site Characterization Analysis of the Site Characterization Report for the Basalt Waste Isolation Project, NUREG-0960 Vol. I, II, U.S. Nuclear Regulatory Commission, Washington, D.C.

NRC (1983c), Final Technical Position on Documentation of Computer Codes for High-Level Waste Management, NUREG-0856, U.S. Nuclear Regulatory Commission, Washington, D.C.

NWTS (1981), NWTS Program Criteria for Mined Geologic Disposal of Nuclear Waste Site Performance Criteria, DOE/NWTS-33(2), National Waste Terminal Storage, U.S. Department of Energy, Washington, D.C.

NWTS (1982a), NWTS Program Criteria for Mined Geologic Disposal of Nuclear Waste, Program Objectives, Functional Requirements, and System Performance Criteria, DOE/NWTS-33(1), National Waste Terminal Storage, U.S. Department of Energy, Washington, D.C.

NWTS (1982b), NWTS Program Criteria for Mined Geologic Disposal of Nuclear Waste, DOE/NWTS-33(3), National Waste Terminal Storage, U.S. Department of Energy, Washington, D.C.

NWTS (1982c), NWTS Program Criteria for Mined Geologic Disposal of Nuclear Waste - Waste Package Functional Requirements and Performance Criteria for Commercial High-Level Waste, DOE/NWTS-33(4a), National Waste Terminal Storage, U.S. Department of Energy, Washington, D.C.

Phelan, D. M., R. M. Taylor, and S. Fricke (1982), "A Maintenance-Free Dissolved Oxygen Monitor," American Laboratory, 14(7).

Plodinec, M. J., G. G. Wicks, and N. E. Bibler (1982), An Assessment of Savannah River Borosilicate Glass in the Repository Environment, DP-1629, E. I. duPont de Nemours and Company, Savannah River Laboratory, Aiken, South Carolina.

PNL (1981), Materials Characterization Center: Test Methods, Preliminary Version, PNL-3990, Pacific Northwest Laboratory, Richland, Washington.

Potter, J. (1981), Experimental Rock-Water Interactions at Temperature to 300°C: Implications for Fluid Flow, Solute Transport, and Silicate Mineral Zoning on Crustal Geothermal Systems, Ph. D. thesis, Stanford University, Stanford, California.

Pusch, R. (1980), Swelling Pressure of Highly Compacted Bentonite, KBS Technical Report 80-13.

Relyea, J. F. (1982), "Theoretical and Experimental Considerations for the Use of the Column Method for Determining Retardation Factors," Radioactive Waste Management and the Nuclear Fuel Cycle.

Rockwell (1982a), Project Management Plan for the Hydrothermal Testing of Waste-Barrier-Rock Interactions Using Fully Radioactive Waste Forms, RSD-BWI-PMP-003, Rockwell Hanford Operations, Richland, Washington.

Rockwell (1982b), "Engineering Procedures Manual," RHO-MA-115, Rockwell Hanford Operations, Richland, Washington.

Rockwell (1983a), Draft Waste Acceptance Requirements for the Basalt Waste Isolation Project, SD-BWI-CR-018, Rockwell Hanford Operations, Richland, Washington.

Rockwell (1983b), Basalt Operations Procedures, RHO-BWI-MA-4, Vol. 1-3, Basalt Waste Isolation Project, Rockwell Hanford Operations, Richland, Washington.

Rockwell (1983c), "BWIP Configuration Management Plan," SD-BWI-CM-001 Rev. A-0, Rockwell Hanford Operations, Richland, Washington.

Rockwell (1984), "Technical Information Manual," RHO-MA-105, Rockwell Hanford Operations, Richland, Washington.

Ross, W. A., D. J. Bradley, L. R. Bunnel, W. J. Gray, Y. B. Katayama, G. B. Mellinger, J. E. Mendel, F. P. Roberts, R. P. Turcotte, J. W. Wald, W. E. Weber, and J. H. Westik, Jr. (1978), Annual Report on the Characterization of High Level Waste Glasses, PNL-2625, Pacific Northwest Laboratory, Richland, Washington.

Salter, P. F., L. L. Ames, and J. E. McGarrah (1981a), Sorption of Selected Radionuclides on Secondary Minerals Associated with the Columbia River Basalts, RHO-BWI-LD-43, Rockwell Hanford Operations, Richland, Washington.

Salter, P. F., L. L. Ames, and J. E. McGarrah (1981b), The Sorption Behavior of Selected Radionuclides on Columbia River Basalts, RHO-BWI-LD-48, Rockwell Hanford Operations, Richland, Washington.

Shaikh, A. V. and D. E. Tallman (1978), "Species - Specific Analysis for Nanogram Quantities of Arsenic in Natural Waters by Arsine Generation followed by Graphite Furance Atomic Absorption Spectrometry," Anal. Chim. Acta 98.

Slate, S. C., W. A. Ross, and W. L. Partain (1981), Reference Commercial High-Level Waste Glass and Canister Definition, PNL-3838, Pacific Northwest Laboratory, Richland, Washington.

Taylor, C. L., G. J. Anttonen, J. E. O'Rourke, and D. Allirot (1980), Preliminary Geochemical and Physical Testing of Materials for Plugging of Man-Made Accesses to a Repository in Basalt, RHO-BWI-C-66, Rockwell Hanford Operations, Richland, Washington.

Thornton, E. C. and W. E. Seyfried, Jr. (1982), "The Sonet Effect: Potential for Thermodiffusional Transport in a Nuclear Waste Repository," Geological Society of America Abstracts with Program 14.

Westerman, R. E. (1983a), Elevated-Temperature Corrosion of Iron-Base Alloys in Hanford Grade Ronde Groundwater, SD-BWI-TI-151, Rockwell Hanford Operations, Richland, Washington.

Westerman, R. E. (1983b), Irradiation-Corrosion of Iron-Base Alloys in Hanford Grande Ronde Groundwater, SD-BWI-TI-140, Rockwell Hanford Operations, Richland, Washington.

Wood, B. J. (1980), Estimation of Waste Package Performance Requirements for a Nuclear Waste Repository in Basalt, RHO-BWI-ST-10, Rockwell Hanford Operations, Richland, Washington.

Wood, B. J. and D. Rai (1981), Nuclear Waste Disposal: Actinide Containment in Geologic Repositories, PNL-SA-9549, Pacific Northwest Laboratories, and RHO-BWI-ST-21 P, Rockwell Hanford Operations, Richland, Washington.

Wood, M. I., J. F. Relyea, D. L. Lane, and R, A. Carlson (1984), Chemical and Physical Properties of Waste Package Packing Materials, SD-BWI-TI-155, Rockwell Hanford Operations, Richland, Washington.

APPENDIX A
STATISTICAL TEST DESIGN

APPENDIX A
STATISTICAL TEST DESIGN

DESIGN STRATEGY

Statistical test design is a proven technique for obtaining fast, accurate results with a minimum of time and effort, particularly when a large number of variables are of potential importance (Cochran and Cox, 1957). In addition, interpretation of the results is simplified; interactions among the variables is seen; and an assessment of the reliability of the data is obtained.

Factorial designs allow simultaneous estimation of the effects of several factors. Experiments are run for all combinations of p factors with ℓ levels per factor. The number of experimental runs (n) is:

$$n = \ell p \qquad \text{(A-1)}$$

Two-level factorial designs ($\ell = 2$) are useful for a wide variety of problems. Experimental designs of this type are easy to plan and analyze, both continuous and discrete factors can be used; and they yield reliable models for response variables that have no strong curvature in the experimental region. However, when the number of factors is greater than approximately six, the number of runs required ($2^6 = 64$) often become impractical. In this case, an appropriate first step would be a screening design which identifies the significant variables.

Most screening designs are obtained by using a fraction of the $2^{p'}$ factorial design. It is important in fractional design that the proper experiments be omitted, for one incorrect omission can lead to a situation in which there is no estimate for the effects of one factor and unnecessary estimates of higher-order interactions. There are several types of screening designs available in the literature (Plackett and Burman, 1946; Box and Hunter, 1961). The Plackett-Burman design is a specific fraction that allows efficient estimation of the effects of the variables under study (Plackett-Burman, 1946). The most useful Plackett-Burman designs are for 12, 20, and 28 runs which handle up to 11, 19, and 27 variables, respectively. There is obviously a tremendous reduction in the number of experiments compared to the Plackett-Burman designs that do not provide estimates of the interactions between variables. However, it should be remembered that the purpose of a screening design is to select a few variables from many so that these few can be investigated in detail. This can be done by using a more complete factorial or a response surface design such as the Box-Behnken (Box and Behnken, 1960).

An example of the 20-run Plackett-Burman screening design is given in Table A-1. The two levels are coded "+" and "-" for the high and low values of the variable, respectively. The variables XI, X2, etc. are across the top of the table. The run numbers are denoted by the column at the left.

TABLE A-1. Twenty-Run Plackett-Burman Design.

Run	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	X_{12}	X_{13}	X_{14}	X_{15}	X_{16}	X_{17}	X_{18}	X_{19}
1	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-
2	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+
3	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+
4	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-
5	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-
6	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+
7	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+
8	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+
9	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+
10	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-
11	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+
12	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-
13	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+
14	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-
15	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-
16	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-
17	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-
18	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+
19	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+
20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

*The high (+) and low (-) values for the variable X.

After completion of the experiments, the first step is to calculate the "factor effect" for each variable. The factor effect is then compared with the experimental error to determine whether or not the variable is significant. This is accomplished as follows:

1. The response value for each run is written to the right of the table.

2. The values of the response corresponding to a plus sign are totaled for each column.

3. The values of the response corresponding to a minus sign are totaled for each column.

4. The sums from Step 3 are subtracted from the sums from Step 2.

5. The difference is divided by the number of plus signs in the columns (in this case, 10). The result is the factor effect for each column. For the extra columns to which no factor is assigned, this number is an estimate of experimental error.

The experimental error is calculated from the Unassigned Factor Effects (UFE) using the equation:

$$S_{FE} = \frac{1}{q} (UFE^2, + UFE^2 + . . . UFE_q^2) \qquad \text{(A-2)}$$

where S_{FE} is the pooled standard deviation of the unassigned factor effects and q is the number of unassigned factor effects. The minimum absolute value (MIN) for the factor effect to be significant at a specified significance level is calculated from:

$$(MIN) = tS_{FE} \qquad \text{(A-3)}$$

where t is obtained from probability tables for different confidence levels and degrees of freedom. The computed factor effect values for each variable are compared with (MIN) and significant factors are identified. The computational analysis also indicates how the significant factor affects the response (increase or decrease response values). To quantify the effects, however, usually requires more detailed investigation of significant variables.

In the 20-run Plackett-Burman design, all 20 results are used in calculating each factor effect. This leads to hidden replication in the experiments. Each effect is a difference between two averages. Because of the hidden replication, most Plackett-Burman designs are not replicated. The improved precision of the factor effects due to hidden replication is given by the precision ratio:

$$\frac{2\ FE}{\partial} = \frac{2}{n} \qquad \text{(A-4)}$$

where:

FE = standard deviation of a factor effect
∂ = standard deviation of a single observation
n = total number of observations in the design (in this case 20).

Once the significant factors have been identified by a screening design, the next step is to describe the response of one or more dependent variable(s) to several independent variables. This relationship can be expressed by one or more mathematical equations or models. Models can be empirical or theoretical. The exact theoretical model is rarely known; therefore, empirical models must be used to approximate the response. Polynomial approximations are widely used and have proven very valuable in modeling. The polynomial model must represent the linear, interaction, and curvature effects with respect to all of the continuous independent variables. The experimental design for developing the models must have at least three levels for each independent variable since curvature effects are to be estimated. It would be feasible to use the full three-level factorial which would provide orthogonal estimates of the linear quadratic and interaction effects. A disadvantage of the full three-level factorial is the large number of experimental runs required ($n = 3^p$ runs). There are, however, a number of designs available that employ a subset of experimental points of the full three-level factorial. The three factor Box-Behnken design (Box and Behnken, 1960), for example, uses 13 of the 27 points from the full factorial with two extra replicates at the center point, for a total of 15 points. Five degrees of freedom are available for estimation of error. This design is shown in Table A-2, where the levels +1, 0, and -1 correspond to high, middle, and low-levels of the variables, respectively. In case extrapolation is required, it is necessary to develop a theoretical model for the purpose. The experimental data form a good basis for developing and fitting the theoretical model. In particular, adequacy of the proposed theoretical model requires, at the least, that it fit the experimental data as precisely as the empirical polynomial model.

Design of Accelerated Aging Tests

It must be demonstrated that waste packages in a nuclear waste repository in basalt will contain the waste for at least 300 yr. As a matter of practicality, barrier materials will be tested over time periods that are extremely short compared to this time period. To demonstrate this

TABLE A-2. Three-Variable Box-Behnken Design.

Run	X_1	X_2	X_3	
1	+1	+1	0	
2	+1	-1	0	
3	-1	+1	0	
4	-1	-1	0	
5	+1	0	+1	
6	+1	0	-1	
7	-1	0	+1	
8	-1	0	-1	
9	0	+1	+1	
10	0	+1	-1	
11	0	-1	+1	
12	0	-1	-1	
13	0	0	0	
14	0	0	0	Center Point
15	0	0	0	

requirement it is essential that accelerated aging experiments be designed to predict the long-term performance of the waste package. A methodology for design accelerated tests has been described (DOE/NWTS, 1982; Thomas and Gaines, 1978).

An accelerated life test is designed to yield a valid prediction of how long the system will continue to operate satisfactorily in the field given that its performance is satisfactory at t = o. Accelerated tests should be designed so that full advantage is taken of the ideas and concepts of statistically designed experiments. The main advantage of using statistically designed experiments is that the number of test conditions (combinations of stresses) can be kept at a minimum without degrading the quality of the analysis of the experimental (overstress) data and affords the opportunity to systematically generate the best set of data for estimating lifetime parameters recognizing limitations on the number of measurements that can be obtained. It has been found, however, that statistically designed experiments seem to be most useful when there is very little known about the expected behavior of the item being tested. The more prior knowledge that exists about the material being tested and, in particular, about the behavior of this material under a variety of conditions, the more difficult it is to statistically design an experiment that incorporates this prior knowledge.

The following brief description of the test methodology was taken from DOE/NWTS (1982). For more details, the previous two references should be consulted.

The first stage in the design of an accelerated test study of a barrier material is concerned with specifications of the material to be tested and the extractions and quantification of engineering judgment relevant to a specific degradation mechanism that is expected to occur under normal operating conditions. This procedure is based on explicit consideration of all combinations of high- and low-levels of all stresses that could be used in the test. As used in this appendix, the term "stress" refers to the action of an external mechanism on the system under investigation; consideration is given, initially, to all such combinations although it is recognized that not all of these combinations will actually be tested in the laboratory. The procedure is initially structured in the form of a complete factorial experimental design to aid in quantifying specific and engineering judgment and to provide a framework for documenting the judgmental process that results in the combinations of stresses that are to be tested. Because of the judgmental basis of this procedure, several iterations may be required to arrive at a satisfactory set of test conditions. The selected set of test conditions (combination of stresses) is represented in the form of a hierarchal tree in which the stress combinations to be tested are associated with terminal points of the branches of the tree.

In summary, this first stage in designing the accelerated test consists of:

1. Conceptually examining the combinations of stresses believed to be relevant to normal operating conditions and potentially usable in accelerated testing.

2. Selecting a subset of these combinations of stresses for actual testing.

3. Representing the selected test conditions as a hierarchal tree.

The higher-than-normal stress levels to be used in testing are coded so that +1 and -1 correspond to the highest and lowest levels, respectively, of each type of stress involved. Quantitative representatives of normal stress conditions are then determined consistent with these coded representations of highest- and lowest-test levels.

The next stage in the test design process consists of representing the hierarchal tree as a multivariate Lagrange polynomial that is a generalization of a method of Hoel and Levine (1964). This generalization is discussed in Gaines et al. (1977). The polynomial representation quantitatively relates the normal stress levels to the higher-than-normal stress levels of the accelerated test, and provides the basis for accelerated test conditions, and the optimum allocation of test specimens among the stress combinations that comprise the test.

In summary, the second stage of accelerated test design process consists of

- Identifying the expected repository conditions believed to affect the life of the material in the field. These conditions constitute normal stress conditions

- Identifying all the expected degradation modes that may affect serviceable life of the material

- For each failure mode, identifying all the stresses (thermal, mechanical, chemical, electrical, radiation, etc.) that may contribute to the degradation of the material in the field

- For each such stress, identifying possible measurement techniques that could be used to measure associated changes in properties of the material

- Identifying the combinations of environmental (repository) conditions together with their associated stresses and identifying a single degradation process that is most likely to be responsible for the "end-of-life" of the material. This degradation process represents the dominant failure mechanism

- For the dominant failure mechanism, identifying all stresses that could affect the degradation rate associated with the dominant failure mechanism. Each of these stresses is quantified so that -1 and +1 denote the lowest and highest levels, respectively, that could be used in an accelerated test. The stress level coded as -1 should be the lowest overstress level that would be expected to yield measurable degradation during the time period allowed for the accelerated test; the stress level associated with +1 should be the highest stress level that is feasible and consistent with the requirement that the anticipated degradation at the highest level would be the result of the same degradation mechanism expected to occur under the normal stress conditions. This determination of high- and low-stress levels initially is done for each stress separately; subsequent examinations of combinations of stresses may cause some respecifications of these levels to insure compliance with the above requirements for combinations of stresses as well as for individual stresses

- Forming a complete factorial design comprised of all possible combinations of high- and low-stress levels

- By means of scientific and engineering judgments, forming a system of ratings for each of the test conditions. These ratings are intended to reflect the relative severities of the associated test conditions, consistent with available scientific and engineering knowledge. Since such information is generally extremely limited, considerable subjectivity is required to produce these ratings. One method of assigning severity ratings to combinations of test conditions that has been found to be useful involves basing the relative severity ratings on the expected percentage changes in degradation rates corresponding to changes from high- to low-levels of stress.

Once the numerical scales for each stress have been defined and the Lagrange polynomial has been extrapolated to the point representing normal stress conditions, the engineering design is then augmented by adding test conditions (removed during pruning) to remove as many of the statistical deficiencies as possible, consistent with test implementation constraints.

After the final test design has been selected, the extrapolation procedure of Hoel and Levine is applied to determine the optimal distributions of material specimens among test conditions. It is a general approach that a minimum of five specimens be used for any one test condition and that a minimum of five stress levels be used for each "important" stress, such as temperature.

To implement the accelerated test the following steps are taken:

- Instrumentation is selected appropriate for each test condition, taking into consideration accuracy, precision, calibration requirements, maintenance, etc.

- The experimental protocol is written detailing the sequence of measurements and data acquisition procedures

- Empirical, statistical, and conceptual methods are used to analyze the data.

The preceding discussion indicates how the general concepts of experimental designs are useful in helping to organize and develop an initial plan for experimentation. The procedure begins with a full factorial design which is subsequently pruned to retain those combinations of test conditions that are most desirable. Also indicated is the general desirability augmenting the engineering tests to improve the statistical properties of the experimental design. Once a suitable design has been identified, however, it should not be automatically concluded that a routine implementation of the design will yield useful results. Indeed, the conditions that are typically assumed to hold for the effective implementation of standard experimental designs tend to be severely violated in accelerated testing.

It must also be recognized that it is not appropriate to assume that all matters involving the reliability or predicted lifetimes of waste package materials may be resolved by carrying out accelerated life tests as described above. However, where such tests are feasible and can lead to probability models from which reliability calculations can be derived to reflect "reasonable assurance," it is essential that such procedures be used. In response to the need for demonstrating "reasonable assurance" that high-level waste packages will meet the U.S. Nuclear Regulatory Commission numerical performance objectives (NRC, 1983) a quantitation reliability program will be developed and included in Section 5.1.4.2., Performance Evaluation, in the first upgrade of this test plan to be completed by September 30, 1984.

REFERENCES

Box, G. E. P. and D. W. Behnken (1960), "Some New Three Level Designs for the Study of Quantitative Variables," Technometrics, 2, pp. 455-75.

Box, G. E. P. and J. S. Hunter (1961), "The 2^{k-p} Fractional Factorial Designs," Technometrics, 3, pp. 311-351.

Cochran, W. G. and G. M. Cox (1957), Experimental Designs, John Wiley & Sons, New York, 2nd Ed, 454 p.

DOE/NWTS-34 (1982), "Guidelines for the Development and Testing of NWTS Waste Package Materials," DOE/NWTS-34, U.S. Department of Energy, Office of NWTS Integration, Battelle Project Management Division, Columbus, Ohio, 214 p.

Gaines, G. B., R. E. Thomas et al. (1977), "Methodology for Designing Accelerated Aging Tests for Predicting Life of Photovoltaic Arrays," Final Report, ERDA/JPL-954328-77/1, U.S. Energy Research and Development Administration and Jet Propulsion Laboratory.

Hoel, P. G. and A. Levine (1964), "Optimal Spacing and Weighting in Polynomial Prediction," Annual of Mathematical Statistics, 2, pp. 1553-1650.

NRC (1093), Nuclear Regulatory Commission, 10 CFR Part 60, Disposal of High Level Radioactive Wastes in Geologic Repositories, Technical Criteria, U.S. Nuclear Regulatory Commission, Washington, D.C., Federal Register, Vol. 48, No. 120, pp. 28194.

Plackett, R. L. and J. P. Burman (1946), "The Design of Optimum Multifactorial Experiments," Biometrika, 33, pp. 305-25.

Thomas, R. E. and G. B. Gaines, "Procedure for Developing Experimental Designs for Accelerated Tests for Service Life Prediction," Presented at the Thirteenth IEEE Photovoltaic Specialists Conference, Washington, D.C.

APPENDIX B
SCIENTIFIC RATIONALE FOR WASTE/BARRIER/ROCK INTERACTION TESTING

APPENDIX B
SCIENTIFIC RATIONALE FOR WASTE/BARRIER/ROCK INTERACTION TESTING

INTRODUCTION

The principal goal of the Basalt Waste Isolation Project (BWIP) is to evaluate the feasibility of permanent storage of nuclear waste in a nuclear waste repository in basalt. This evaluation must be based on regulatory criteria (NRC, 1983; EPA, 1982) that determine the required long-term performance of a nuclear waste repository in basalt. These performance criteria must be used to evaluate the performance required of the engineered barrier system. The geologic (natural) barriers of the repository site plus the engineered barrier system (waste package plus underground facility) comprise the total barrier to release of materials to the accessible environment. Where the natural barriers of the repository itself cannot meet or exceed the regulatory criteria, the performance of engineered barriers must supplement the performance of the geologic barriers to insure regulatory compliance and isolation of waste materials.

DISCUSSION

The BWIP and the National Waste Terminal Storage (NWTS) Program have adopted an approach to evaluating long-term barrier performance that relies on site-specific, hydrothermal testing of waste package components, both individually and as an integrated assembly (NWTS, 1981).

It is neither economically nor experimentally feasible to conduct such hydrothermal tests for durations approaching containment times (300 yr to 1,000 yr) demanded in current regulatory criteria. It is, therefore, imperative that a reliability program and expert scientific judgment guide the design and interpretation of such a testing program. Laboratory tests, coupled with expert scientific judgement and reliability analysis, are key to the meaningful extrapolation of short-term laboratory data to the much longer time periods expected during the functional life of a nuclear waste repository in basalt.

This extrapolation of results from barrier material testing to long-term performance is closely allied to the common dilemma encountered by geoscientists who attempt to extrapolate similar laboratory data (tests of less than 2 yr duration) to natural geochemical and mineralogic processes that occur over hundreds to millions of years. Geochemists and experimental petrologists have accordingly developed several theories, based on chemical thermodynamic and kinetic reaction principles, to address this extrapolation problem. These theories have been validated by observation of repeated agreements between theoretical predictions and observed natural examples in a variety of geochemical systems. These interpretive theories, already in common use by the geochemical community, should serve as the basis for the expert judgment regarding extrapolation of waste/barrier/basalt test results to time scales appropriate to regulatory isolation criteria.

The long-term stability and performance of candidate barrier materials are chiefly, though not exclusively, determined by their chemical interaction with the groundwaters that will eventually fill the repository. The dominant process for hydrothermal interactions in the waste/barrier/basalt system is gradual dissolution of coexisting primary solid phases. Dissolution will be accompanied by precipitation and growth of an assemblage of secondary alteration phases that are more stable under the given repository conditions. These dissolution and precipitation processes represent an overall irreversible reaction (Helgeson, 1968; Giggenbach, 1981) that may be summarized by the expression:

$$\text{Solution}_{\text{initial}} + \text{Primary (unstable) Phases}$$

$$\text{Solution}_{\text{final}} + \text{Secondary (stable) Phases.}$$

The Ostwald step rule is a useful, albeit empirical, observation from natural and experimental studies of hydrothermally altered rocks (Fyfe and Verhoogen, 1958). It states that the transition from an unstable to a stable phase(s) generally occurs through the formation of a series of intermediate metastable phases, and that the thermodynamic instability of these intermediate phases will decrease as the reaction progresses. The thermodynamic parameter measuring the relative stability of a phase in a hydrothermal system is its free energy, that is, the total driving force for reaction between solids and solution. This free energy is also a direct measure of solubility of a solid phase (Garrels and Christ, 1965; Giggenbach, 1981). The relative hydrothermal stability of phases, therefore, can be determined directly from relative solubilities (i.e., the more soluble phase will be the least stable). At any point during a stepwise alteration reaction process, the composition of the solution will be governed by the relative solubilities of coexisting phases.

In the limiting case, in which only the most stable solid phases are present, solubility data can be measured directly from solution composition (Wood and Rai, 1981; Rai et al., 1981) or evaluated from thermodynamic data, when available (Pourbaix, 1966; Garrels and Christ, 1965). It is important to stress that such solubility data are defined to be independent of time and reaction pathway because of the assumed equilibrium nature of the system. Because all chemical systems evolve toward equilibrium (i.e., an assemblage of stable phases), and because of the very low flow rates of groundwater expected in a nuclear waste repository (NWTS, 1981; MCC, 1981; Arnett et al., 1981), the use of solubility limits models to predict long-term release rates of radionuclides from a waste package/repository system is justifiable.

The application of thermodynamic solubility constraints can be extended to a more general model for hydrothermal reactions between solution and metastable solids. A schematic representation of the measured solution concentration as a function of time (experiment duration) in a hydrothermal system is presented in Figure B-1. In this case, there is assumed to be a solid phase in solution that is metastable relative to one (or more)

The long-term stability and performance of candidate barrier materials are chiefly, though not exclusively, determined by their chemical interaction with the groundwaters that will eventually fill the repository. The dominant process for hydrothermal interactions in the waste/barrier/basalt system is gradual dissolution of coexisting primary solid phases. Dissolution will be accompanied by precipitation and growth of an assemblage of secondary alteration phases that are more stable under the given repository conditions. These dissolution and precipitation processes represent an overall irreversible reaction (Helgeson, 1968; Giggenbach, 1981) that may be summarized by the expression:

$$\text{Solution}_{\text{initial}} + \text{Primary (unstable) Phases}$$

$$\text{Solution}_{\text{final}} + \text{Secondary (stable) Phases.}$$

The Ostwald step rule is a useful, albeit empirical, observation from natural and experimental studies of hydrothermally altered rocks (Fyfe and Verhoogen, 1958). It states that the transition from an unstable to a stable phase(s) generally occurs through the formation of a series of intermediate metastable phases, and that the thermodynamic instability of these intermediate phases will decrease as the reaction progresses. The thermodynamic parameter measuring the relative stability of a phase in a hydrothermal system is its free energy, that is, the total driving force for reaction between solids and solution. This free energy is also a direct measure of solubility of a solid phase (Garrels and Christ, 1965; Giggenbach, 1981). The relative hydrothermal stability of phases, therefore, can be determined directly from relative solubilities (i.e., the more soluble phase will be the least stable). At any point during a stepwise alteration reaction process, the composition of the solution will be governed by the relative solubilities of coexisting phases.

In the limiting case, in which only the most stable solid phases are present, solubility data can be measured directly from solution composition (Wood and Rai, 1981; Rai et al., 1981) or evaluated from thermodynamic data, when available (Pourbaix, 1966; Garrels and Christ, 1965). It is important to stress that such solubility data are defined to be independent of time and reaction pathway because of the assumed equilibrium nature of the system. Because all chemical systems evolve toward equilibrium (i.e., an assemblage of stable phases), and because of the very low flow rates of groundwater expected in a nuclear waste repository (NWTS, 1981; MCC, 1981; Arnett et al., 1981), the use of solubility limits models to predict long-term release rates of radionuclides from a waste package/repository system is justifiable.

The application of thermodynamic solubility constraints can be extended to a more general model for hydrothermal reactions between solution and metastable solids. A schematic representation of the measured solution concentration as a function of time (experiment duration) in a hydrothermal system is presented in Figure B-1. In this case, there is assumed to be a solid phase in solution that is metastable relative to one (or more) compositionally related solid phase. Note that this more stable phase is not necessarily the most stable of all compositionally related phases. At time t_0 a solution in contact with the initial metastable phase will be undersaturated with respect to the dissolving chemical component that is measured. At this point the entire free energy of the hydrothermal reaction of the solid with solution will be available to drive the dissolution process. The initial rate of dissolution ("leaching"), i.e., the change in solution composition with time, will be extremely high as represented by the tangential slope drawn at time t_1 in Figure B-1. As the concentration of the dissolved component increases, at time t_2, the available free energy to drive the dissolution decreases, with a concomitant decrease in "leach rate" (i.e., a more gentle slope of the line tangential at time t_2 in Fig. B-1). Eventually at time t_c, assuming no precipitation of new, more stable solid phases, the solution reaches a metastable equilibrium concentration (solubility limit, at time t_3 in Fig. B-1) of the dissolved component, and the "leach rate" is zero. It is important to stress that while the "leach rate" is zero, combined dissolution and precipitation of the metastable phase continues at equilibrium.

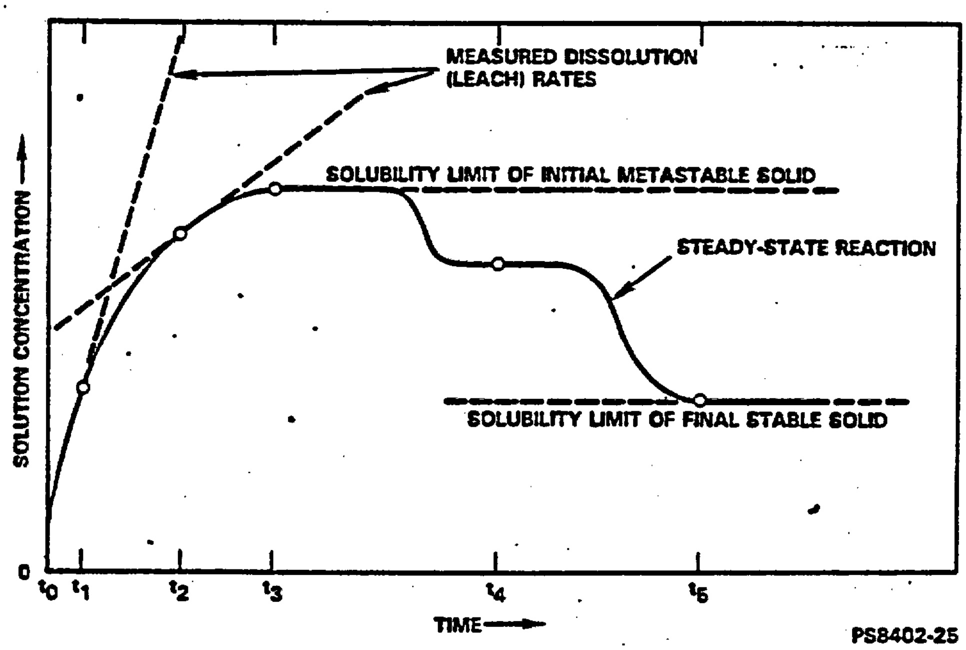


FIGURE B-1. Schematic Illustration of Solution Concentration as a Function of Time for a Hypothetical Waste/Barrier/Rock Hydrothermal Reaction.

Parabolic dissolution rates, as portrayed in Figure B-1, have been characteristically interpreted in dissolution* studies as indicating that diffusion through a leached surface layer is the rate-controlling step. It has recently been demonstrated, however, that observed parabolic time dependencies for dissolution of minerals can be artifacts of precipitation of secondary phases (Holdren and Adams, 1982), time-dependent, surface detachment processes (Dibble and Tiller, 1981b), or sample preparation methods (Grandstaff, 1980; Schott et al., 1981). Although there is clear evidence of a leach layer on hydrothermally reacted glass waste forms (e.g., McVay et al., 1981) the possibility remains that observed parabolic dissolution rates for glass waste forms may be the results of several parabolic rate processes. Clearly, the use of experimental "leach rates," which strongly vary as a function of time, can lead to overly pessimistic and thermodynamically unjustified interpretations of the dissolution behavior and stability limits of solids in the presence of slow-flowing or static solutions. The measured solubility of a phase in hydrothermal solution will better represent the true stability of that phase as well as the maximum concentration of dissolved components.

Because the equilibrium represented at time t_3 is stated to be metastable, there is a probability of precipitation of new, successively more stable phases. As a new, more stable phase nucleates and begins to grow, the dissolution rate of the less stable phase and the concurrent growth rate of the more stable coexisting phase are opposing processes seeking to establish their own solubility control of solution composition (Holloway et al., 1981; Apted, 1981; Berner, 1978; Mottl and Holland, 1978; Lasaga, 1981).

For example, if the irreversible dissolution of an unstable phase such as glass is rapid relative to the growth of a more stable alteration phase, the solution composition will reflect mainly the solubility of the glass (for equal areas of glass and alteration phase). If the relative reaction rates were reversed so the alteration phase grows much faster than the primary phase dissolves, then the bulk solution composition will be determined primarily by the solubility of the alteration phase (Berner, 1980; Dibble and Tiller, 1981a). Intermediate, steady-state reactions (note, these are not equilibrium reactions) exist between these extremes (at time t_4, Fig. B-1). These reactions represent a balancing of the rates at which chemical components are being dissolved from unstable primary phases and the rates at which the same components are removed from solution into more stable, secondary phases. Steady-state conditions will eventually change with time, as more stable phases nucleate and grow or unstable phases become totally consumed. This, in turn, may cause the solution to attain new steady-state compositions. The concentration of dissolved components represented by these evolving steady-state reactions must decrease with reaction progress (i.e., longer periods of time) because each new phase must

*Solution concentrations above this solubility limit can occur but are exceptional, transitory events. They will be dismissed from this elementary discussion.

be more stable, hence less soluble, than the previous phases. Eventually a true equilibrium solid (or assemblage of solids) will form (at time t_5, Fig. B-1), representing the solubility limiting case previously discussed. It can be expected, therefore, that if hydrothermal tests are conducted for durations sufficient to attain a steady-state reaction, these data will provide conservative radionuclide release rates relative to equilibrium solubility expected to control the actual long-term release rates.

The length of time needed to attain steady-state (or solubility-limited) concentrations in static, hydrothermal tests at expected repository conditions could, in some cases, be greater than that feasible for laboratory testing. In these instances, these dissolution and growth rates are functions of several variables (Dibble and Tiller, 1981b), including temperature, reaction activation energy, reactive surface area (or reactive surficial mass), solution concentrations, and the available free energy of the system, which is the difference in free energy (or solubility) between the unstable reacting phase(s) and the stable product phase(s). This kinetic model, based on the energetics and mechanisms controlling dissolution and growth processes, serves as the justification for a variety of experimental techniques that can be adopted to actually accelerate the test. By speeding up the rates of dissolution and growth, the results of short-duration laboratory tests can be made to approach a state of reaction identical to that achieved in nature over much longer time periods.

The Interface Working Group on Accelerated Testing (DOE/NWTS, 1981), for example, has suggested that increasing the temperature of laboratory tests can dramatically increase the reaction rates of hydrothermal interaction tests on waste package components. This same technique is in common use in chemical engineering technology (e.g., Boudart, 1968) and in geochemical/petrological research (e.g., Mottl and Holland, 1978). The assumption that the same dissolution/growth mechanisms are operative at both high and low hydrothermal temperature is, however, often not justified. This is particularly true for hydrothermal studies of glass reactions, which apparently are dominated initially at low temperature (250°C) by ion exchange (surface leaching) (White et al., 1980) and controlled at high temperature (200°C) by matrix dissolution (Karkhanis et al., 1980).

Standard experimental studies of alteration products and resultant water chemistry of basalt/water reactions utilize powdered samples of basalt (e.g., Seyfried et al., 1979, 1981; Mottl and Holland, 1978). The accepted rationale for this procedure is that by effectively increasing the reactive surface area (or surficial mass) of the basalt, relative to the mass of coexisting solution, the time required for reaction and formation of new solid phases is greatly expedited. For powdered samples, the high surface areas-to-mass ratio of the sample ensures that the entire mass added will be the effective reactive surficial mass. Uncertainty in estimating reactive surficial mass of monoliths, and uncontrollable changes in this parameter because of cracking, create problems of interpreting or extracting meaningful kinetic data from dissolution or solubility tests.

Finally, it has been shown recently that nonthermodynamic parameters such as porosity and permeability (i.e., flow rate) may affect the alteration mineral assemblage produced in hydrothermal systems (Dibble and Tiller, 1981a). High flow rates of solution through a rock system thoroughly mix interface and bulk solutions, permitting a relatively greater portion of the available free energy of the system to be used in surface detachment and attachment processes. This increases the rates of dissolution and growth, resulting in more rapid formations of most of the stable phases (Dibble and Tiller, 1981b). The great advantage of this technique is that use of variable flow rate to accelerate kinetic reaction rates will not involve any change in the operative reaction mechanism.

CONCLUSIONS

The current use of nonflowthrough (static) tests in the rocker-type autoclaves for the bulk of the experimental program is justified by lower cost, simplicity of operation, greater experimental control, and the relatively slow rates of solution flow in natural rock (10^{-3} compared to 10^{-5} flow in a rocker-type autoclave). Flowthrough hydrothermal autoclaves are, however, being developed and constructed by the BWIP. The freedom to vary flow rate and temperature with minimal loss of scientific relevance between experiments will permit a thorough examination of alteration under hydrothermal conditions, minimizing the need for long experiments. Results obtained by promoting rapid attainment of more stable phases using high flow rates are applicable to the long-term performance of a waste package located in a nuclear waste repository in basalt.

REFERENCES

Apted, M. J. (1981), "Hydrothermal Reactions in the System Waste Form/Basalt/Groundwater", in Proceedings of the 1981 National Waste Terminal Storage Program Information Meeting, DOE/NWTS-15, Office of NWTS Integration, Battelle Memorial Institute, Columbus, Ohio, pp. 289-293.

Arnett, R. C., R. D. Mudd, R. G. Baca, M. D. Martin, W. R. Norton, and D. B. McLaughlin (1981), Pasco Basin Hydrologic Modeling and Far-Field Radionuclide Migration Potential, RHO-BWI-LD-44, Rockwell Hanford Operations, Richland, Washington, 68 p.

Berner, R. A. (1978), Rate Control of Mineral Dissolution Under Earth Surface Conditions, American Journal of Science 178, pp. 1235-1252.

Berner, R. A. (1980), Early Diagenesis, Princeton University Press, Princeton, New Jersey, 241 p.

Boudart, M. (1968), Kinetics of Chemical Processes, Prentice-Hall, New York, New York.

Dibble, W. E., Jr. and W. A. Tiller (1981a), "Non-Equilibrium Water/Rock Interactions. I. Model for Interface Controlled Reactions," Geochimica et Cosmochimica Acta, Vol. 45, pp. 79-92.

Dibble, W. E. and W. A. Tiller (1981b), "Kinetic Model of Zeolite Paragenesis in Tuffaceous Sediments," Clay and Clay Minerals, Vol. 29, No. 5, pp. 323-330.

DOE/NWTS (1981), Nuclear Waste Package Materials Degradation Modes and Accelerated Testing, DOE/NWTS-13, Office of NWTS Integration, Battelle Memorial Institute, Columbus, Ohio, 95 p.

EPA (1982), "Environmental Protection Agency, 40 CFR Part 191, Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes," U.S. Environmental Protection Agency, Washington, D.C., Federal Register, 47, (250): pp. 58195.

Fyfe, W. S. and J. Verhoogen (1958), "Kinetics of Metamorphic Reactions," in Metamorphic Reactions and Metamorphic Facies, Fyfe, W., Turner, F., and Verhoogen, J., Eds., Geological Society of America Memoir 73, pp. 53-104.

Garrels, R. M. and C. L. Christ (1965), Solutions, Minerals, and Equilibria, Freeman, Cooper and Company, San Francisco, California, 450 p.

Giggenbach, W. F. (1981), "Geothermal Mineral Equilibria," Geochimica et Cosmochimica Acta, Vol. 45, pp. 393-410.

Grandstaff, D. E. (1980), "The Dissolution Rate of Forsterite Olivine from Hawaiian Beach Sand," in Proceedings, International Symposium on Water-Rock Interactions, B. Hitchon, Ed., Alberta Research Council, Edmonton, Canada, pp. 72-73.

Helgeson, H. C. (1968), "Evaluation of Irreversible Reactions in Geochemical Processes Involving Minerals and Aqueous Solutions--I. Thermodynamic Relations," Geochimica et Cosmochimica Acta, Vol. 32, pp. 853-877.

Holdren, G. R. and J. E. Adams (1982), "Parabolic Dissolution Kinetics of Silicate Minerals: An Artifact of Nonequilibrium Precipitation Processes," Geology 10, pp. 186-190.

Holloway, J. R., D. M. Jenkins, J. F. Kacoyannakis, and M. J. Apted (1981), The Geochemical Behavior of Supercalcine Waste Form: Its Stability in a Basalt Environment, RHO-BWI-C-105, Arizona State University for Rockwell Hanford Operations, Richland, Washington, 45 p.

Karkhanis, S. N., G. M. Bancroft, W. S. Fyfe, and J. D. Brown (1980), "Leaching Behavior of Rhyolite Glass," Nature, Vol. 284, pp. 435-437.

Lasaga, A. C. (1981), "Rate Laws of Chemical Reactions," Kinetics of Geochemical Processes, Lasaga, A. C. and Kirkpatrick, R. J., Eds., Vol. 8 of Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C., pp. 1-68.

Materials Characterization Center (1981), A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms, PNL-3802, Pacific Northwest Laboratory, Richland, Washington, 185 p.

McVay, G. L., D. J. Bradley, and J. F. Kircher (1981) Elemental Release from Glass and Spent Fuel, ONWI-275, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 58 p.

Mottl, M. J. and H. D. Holland (1978), Chemical Exchange During Hydrothermal Alteration of Basalt by Seawater--I. Experimental Results for Major and Minor Components of Seawater," Geochimica et Cosmochimica Acta, Vol. 42, pp. 1103-1117.

NRC (1983), Nuclear Regulatory Commission, 10 CFR Part 60, Disposal of High-Level Radioactive Wastes in Geologic Repositories, Technical Criteria, U.S. Nuclear Regulatory Commission, Washington, D.C., Federal Register, Vol. 48, No. 120, p. 28194.

NWTS (1981), NWTS Program Plan for the Development and Testing of NWTS Waste Package Materials, Vol. I and II, DOE/NWTS-34, National Waste Terminal Storage, Office of Nuclear Waste Isolation, Columbus, Ohio, 214 p.

Pourbaix, M. (1966), Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, Oxford, England, 644 p.

Rai, D., R. G. Strickert, R. W. Fulton, G. L. McVay (1981) Neptunium Concentrations in Solutions Contacting Actinide-Doped Glass, PNL-SA-9699, Pacific Northwest Laboratory, Richland, Washington, 22 p.

Seyfried, W. E., Jr. and J. L. Bischoff (1981), "Experimental Seawater-Basalt Interaction at 300°C, 500 Bars, Chemical Exchange, Secondary Mineral Formation and Implication for the Transport of Heavy Metals," Geochimica et Cosmochimica Acta, Vol. 45, pp. 135-147.

Seyfried, W. E., Jr., P. C. Gordon, and F. W. Dickson (1979), "A New Reaction Cell for Hydrothermal Solution Equipment," American Mineralogist, Vol. 64, pp. 646-649.

Schott, J., R. A. Berner, and E. L. Sjoberg (1981), "Mechanism of Pyroxene and Amphibole Weathering-I. Experimental Studies of Iron-Free Minerals," Geochim. Cosmochim. Acta 45, pp. 2123-2135.

White, A. F., H. C. Claassen, and L. V. Benson (1980), The Effect of Dissolution of Volcanic Glass on the Water Chemistry in a Tuffaceous Aquifer, Rainier Mesa, Nevada, U.S. Geological Survey Water-Supply Paper 1535-Q.

Wood, B. J. and D. Rai (1981), Nuclear Waste Isolation: Actinide Containment in Geologic Repositories, RHO-BWI-SA-143/PNL-SA-9549, Rockwell Hanford Operations/Pacific Northwest Laboratory, Richland, Washington, 31 p.

APPENDIX C
APPROACH TO WASTE/BARRIER/ROCK INTERACTION TESTING

APPENDIX C
APPROACH TO WASTE/BARRIER/ROCK INTERACTION TESTING

The Basalt Waste Isolation Project (BWIP) approach to waste/barrier/rock testing is predicated on three assumptions. These are:

- Applicability of experimentally determined solubility (or steady-state) concentration limits for calculation for long-term radionuclide release rates to the very-near-field waste package environment.

- Sequential penetration of groundwater through the engineered barriers of the waste package.

- Fate-of-the-radionuclides, not only during initial release from the waste form, but also during subsequent reaction of radionuclides with other barrier materials and host basalt.

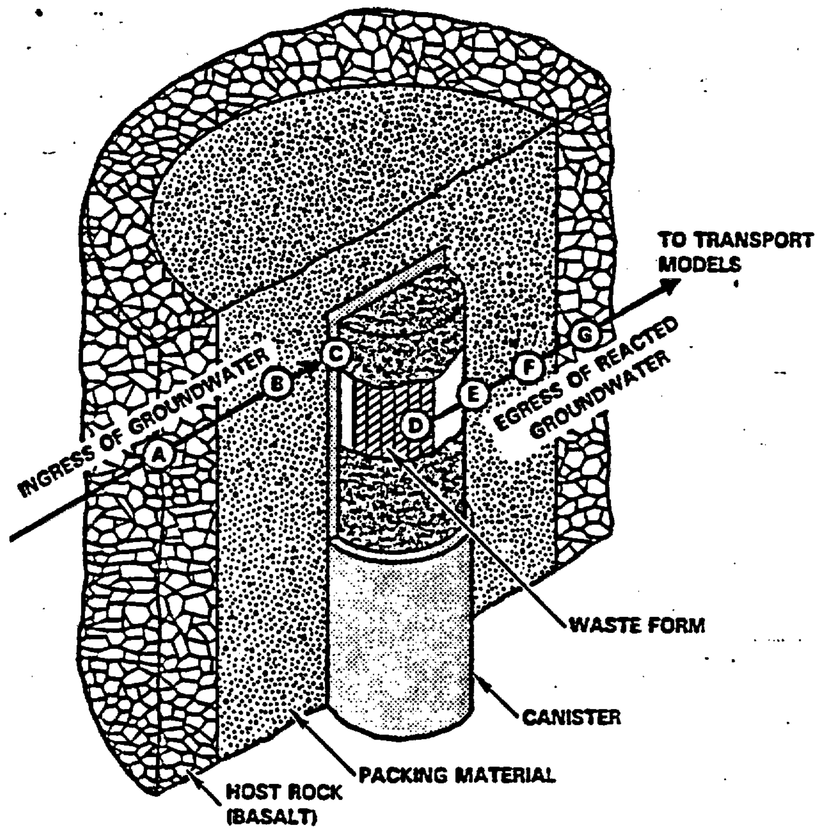
Together these considerations provide an initial identification of what data must be collected and how to best collect these data.

Previous hydrothermal testing on waste forms emphasized the collection of short-term, time-dependent, leach rate data (e.g., Friedman et al., 1980; McVay et al., 1981). Unfortunately, while leach rate data might be used to discriminate the kinetic dissolution behavior of different waste forms, such short-term, time-dependent data have questionable applicability to long-term (100 yr) performance assessment of a waste form in a repository environment (Savage and Robbins, 1982; Gambow, 1982; Apted, 1982).

Is has been argued (Wood, 1980; Wood and Rai, 1981; Apted, 1982; Chambre et al., 1982) that time-independent solubility limits or steady-state reactions* are more appropriate and useful data for evaluating long-term radionuclide release rates from waste packages. This is particularly true for slow flow rate conditions expected in the very-near-field environment of a nuclear waste repository in basalt (DOE-RL, 1982). The scientific justification for this testing approach, based on solubility/steady-state concentration limits to release, is developed more fully in this appendix. The BWIP has endorsed the concept of a sequential hydrothermal testing program for waste package barrier materials (Smith et al., 1980), based on the progressive penetration of barriers by intruding groundwaters (Fig. C-1). This approach emphasizes early hydrothermal stability testing of individual waste package components, including the waste form, and on the composition of coexisting solutions under site-specific repository conditions. Results from these early tests, in turn, are compared with results on successively more complex hydrothermal

---

*Under steady-state reaction conditions, solution compositions are controlled by simultaneous dissolution and growth of primary and secondary (alteration) solid phases, respectively (Mottl and Holland, 1978; Apted, 1982).



INTERACTIONS RELATED TO THE CONTAINMENT PERIOD	INTERACTIONS RELATED TO THE SLOW RELEASE PERIOD
A BASALT + WATER (SITE)	D WASTE + WATER (C)
B PACKING + WATER (A)	E WASTE + CANISTER + WATER (D)
C CANISTER + WATER (B)	F WASTE + CANISTER + PACKING + WATER (E)
	G WASTE + BASALT + WATER (F)

RCP8207-151B

FIGURE C-1. Hydrothermal Interactions Resulting From Groundwater Flow Through a Waste Package.

interaction tests of multiple waste package components. Data from these earlier tests serve also as input into later tests to model more realistically the chemical evolution of hydrothermal reactions within the waste package.

This stepwise, or sequential, approach enables the test program not only to isolate chemical degradation reactions specific to individual waste package components, but also to identify synergistic effects that may develop between the components of the waste package subsystem, as required in 10 CFR 60 (NRC, 1983). These data fulfill design criteria requirements for justifying the need of specific barriers, and, more importantly, establish that barriers are compatible and the presence of one does not degrade the function of another. For example, McVary and Buckwalter (1983) have demonstrated a significant change in the dissolution characteristics of borosilicate glass due to the absence or presence of low-carbon steel. Apted and Myers (1982) have shown that there are significant differences in the alteration solids formed from hydrothermal reaction of both spent fuel and borosilicate glass, depending on whether basalt is present or not. The differences in alteration solids also account for the differences between the steady-state concentrations of several key elements in these same tests.

The current regulatory performance objectives governing waste package design are written, in part, in terms of release rates of radionuclides from the engineered barrier system (NRC, 1983). Previous test programs have emphasized waste form/water tests to supply such release rate information. Actual radionuclide release rates, however, are controlled both by waste form dissolution and by reaction of radionuclide-bearing solutions with other barrier materials. The BWIP waste/barrier/rock interaction test program is oriented toward holistic fate-of-radionuclide studies that address both of these processes.

Based on the principles of solubility/steady-state limits, sequential penetration of barriers, and the fate-of-the-radionuclides the BWIP Waste Package Program has defined three broadly related test methodologies for providing long-term radionuclide release rate data. These are:

- Tracer- and fully radioactive waste/barrier/rock interaction tests performed under static (no flow) conditions
- Radionuclide-doped water/barrier/rock interaction tests performed under static (no flow) conditions
- Tracer- and fully radioactive waste/barrier/rock interaction tests performed under dynamic (flowthrough) conditions.

REFERENCES

Apted, M. J. (1982), "Overview of Hydrothermal Testing of Waste Package Barrier Materials at the Basalt Waste Isolation Project," RHO-BWI-SA-228 P, Rockwell Hanford Operations, Richland, Washington, 21 p.

Apted, M. J. and J. Myers (1982), "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, 78 p.

Chambre, P. L., H. Pigford, and S. Zavosky (1982) "Solubility-Limited Dissolution Rate in Groundwater," ULB-NE-4016, University of California at Berkeley, Berkeley, California, 6 p.

DOE-RL (1982) "Site Characterization Report for the Basalt Waste Isolation Project," DOE-RL 82-3, Rockwell Hanford Operations for the U.S. Department of Energy, Washington, D.C., 2,000 p.

Friedman, A. M., D. J. Lam, and M. G. Seitz (1980), "Summary-Workshop Recommendations, Argonne National Laboratory Specialists Workshop on Basic Research Needs for Nuclear Waste Management," Nuclear Technology, 51, p. 201.

Gambow, B. (1982), "The Role of metal Ion Solubility in Leaching of Nuclear Waste Glasses," in Scientific Basis for Nuclear Waste Management, W. Lutze, Ed., North Holland, New York, New York, pp. 93-102.

McVay, G. L. and C. O. Buckwalter (1983), "Effect of Iron on Waste-Glass Leaching," J. of AM. Ceramic Soc., pp. 66, 170-174.

McVay, G. L., D. J. Bradley, and J. F. Kircher (1981), "Elemental Release from Glass and Spent Fuel," ONWI-275, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 58 p.

Mottl, M. J. and H. D. Holland (1978), "Chemical Exchange During Hydrothermal Alteration of Basalt by Seawater. I. Experimental Results for Major and Minor Components of Seawater," Geochim. Cosmochim. Acta, 42, p. 1103

NRC (1983), Nuclear Regulatory Commission, 10 CFR part 60, Disposal of High Level Radioactive Wastes in Geologic Repositories, Technical Criteria, U.S. Nuclear Regulator Commission, Washington, D.C., Federal Register, Vol. 48, No. 120, p. 28194.

Savage, D. and J. E. Robbins (1982), "The Interaction of Borosilicate Glass and Granodiorite at 100°C, 50 MPa: Implications for Models of Radionuclide Release," W. Lutze, Ed., Scientific Basis for Radioactive Waste Management, Vol. V, Elsevier Science Publishing Co., New York, pp. 145-152.

Smith, M. J., G. J. Anttonen, G. S. Barney, W. E. Coons, F. N. Hodges, R. G. Johnson, J. D. Kaser, R. M. Manabe, S. C. McCarel, E. L. Moore, A. F. Noonan, J. E. O'Rourke, W. W. Schulz, C. L. Taylor, B. J. Wood, and M. I. Wood (1980), "Engineered Barrier Development for a Nuclear Waste Repository Located in Basalt, RHO-BWI-ST-7, Rockwell Hanford Operations, Richland, Washington, 215 p.

Wood, B. J. (1980), "Estimation of Waste Package Performance Requirements for a Nuclear Waste Repository Located in Basalt," RHO-BWI-ST-10, Rockwell Hanford Operations, Richland, Washington, 45 p.

Wood, B. J. and D. Rai (1981), "Nuclear Waste Disposal: Actinide Containment in Geologic Repositories," PNL-SA-9549, Pacific Northwest Laboratory, Richland, Washington and RHO-BWI-SA-143, Rockwell Hanford Operations, Richland, Washington, 31 p.

APPENDIX D
TEST AND ANALYTICAL EQUIPMENT REQUIREMENTS FOR WASTE/BARRIER/ROCK TESTING

APPENDIX D
TEST AND ANALYTICAL EQUIPMENT REQUIREMENTS FOR WASTE/BARRIER/ROCK TESTING

For the waste/barrier/rock interactions testing program, the most appropriate apparatus available for hydrothermal testing is the Dickson sampling autoclave (Dickson et al., 1963; Seyfried and Bischoff, 1979). This apparatus consists of a reaction cell made of gold, contained in a pressure vessel which is externally heated by an electric furnace (Fig. D-1). The aqueous fluid can be sampled at the pressure and temperature of the experiment at any point during the test.* Quench solutions and reacted solids can also be obtained at the conclusion of each experiment. The entire assembly of reaction vessel plus furnace is agitated, either by a rolling or rocking motion, to accelerate reaction rates. The chemical inertness of the inner gold cell, the agitated motion of the assembly, and the ability to sample solutions during the experiment makes the Dickson autoclave ideal for monitoring and interpreting hydrothermal reactions as a function of time.

Low-temperature (100°C) tests place less demands on hydrothermal test equipment, particularly by greatly decreasing the deleterious effects of temperature quenching before taking solution samples. Accordingly, there are several other types of inexpensive reaction vessels that may be usefully employed for proposed doped-groundwater/barrier/rock hydrothermal tests at 90°C. The Materials Characterization Center has developed a Teflon container that can be used to encapsulate combinations of waste package components, allowing the entire container to be placed into a controlled temperature oven (MCC, 1981). Difficulties with the mass transport of CO_2, O_2, H_2, and H_2O through the Teflon walls, however, make such containers less then ideal for long-term (6-month) testing. The Savannah River Laboratory in conjunction with the BWIP is currently developing sealable reaction vessels made of basalt cores for testing with defense high-level waste glasses. Alternately, titanium metal reaction vessels, with simple screw-mounted closure heads and deformable pressure seals, provide a high degree of system inertness over a much higher temperature range than for Teflon

*This feature is important because non-sampling, conventional autoclave systems must be cooled down to below 100°C before a liquid solution sample can be made. Because the solution and solids remain in contact during this cooling down or 'quench' period, significant and undesirable retrograde reaction often occurs as new equilibria conditions are imposed by changing temperature. This retrograde reaction destroys the chemical identity of the actual solution coexisting with the solids at the designed experimental conditions of the test.

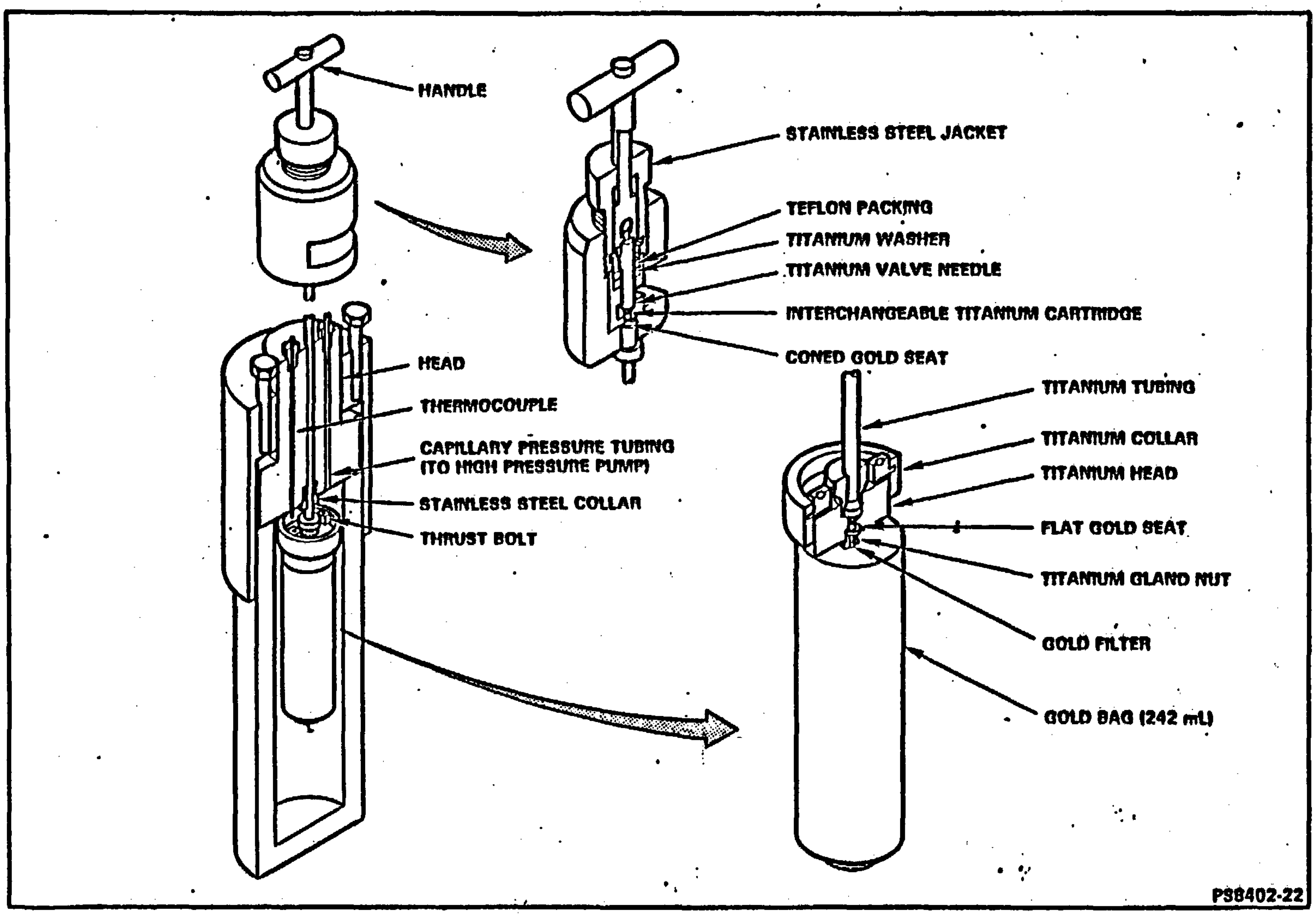


FIGURE D-1. Dickson-Type Sampling Autoclave.

reaction vessels. The advantages of these types of vessels, compared to, say, the Dickson autoclave system, are their lower initial purchase costs, lower labor and maintenance required during testing, and wide commercial availability.. Their disadvantages include the more limited range of operation (pressure/temperature), and the possibility of retrograde quench reactions occurring during cooling and before sampling of hydrothermal solutions.

The flow-through autoclave system (Fig. D-2) uses stainless steel tubes lined with inert material (gold, titanium, or Teflon) as the primary reaction vessel. Powdered waste/barrier/rock materials are packed into the column, which is placed into a controlled temperature furnace. A series of computer-operated pumps and valves provide controlled flow through the packed column at flow rates between 5 x 10^4 m/yr to 0.05 m/yr. Expected repository flow rates are estimated (DOE-RL,.1982) to be slightly to significantly lower than this. It should be reiterated, however, that the principal reasons for performing flow-through studies are the ability to produce the correct sequential penetration of barriers by groundwater, the determination of radionuclide release rates (steady-state concentrations) as a function of flow rate, and the capability of greatly accelerating the reaction rates in short-duration tests.

Techniques for controlling or monitoring pH and Eh in solutions at temperatures below 300°C have been developed (MacDonald, 1978; Niedrach, 1980; Danielson, 1980) and are currently being modified to be compatible with Dickson-type autoclaves. Measured ratios of dissolved redox couples (Cherry et al., 1979; Jacobs and Apted, 1981) may also be used to compute the Eh conditions of sampled test solutions. The program for developing these Eh and pH probes has been presented in Section W.5.1.2.1.

A variety of chemical analyses are required to characterize both solid and aqueous samples. A detailed review of the analytical equipment needed for adequate chemical and crystallographic characterization of hydrothermal solutions and solid reaction products has been presented previously (Apted, 1982, 1983). A short synopsis is presented here.

A complete inventory of both cationic and anionic aqueous species concentrations must be determined. This is because the formation of highly soluble solution complexes of radionuclide and the formation of radionuclide-bearing alteration solids will both be strongly controlled by the concentration of other nonradioactive elements in the groundwater. Room temperature pH values must be coupled with total concentration data on dissolved acid-base solution species and charge balance considerations to recalculate the solution speciation and pH value at the temperature conditions of the test. Selective ion determination, for dissolved elements with multiple oxidation states, may be required to evaluate the prevailing Eh conditions of the solution, as buffered by the reactive solids. The concentrations of many dissolved radionuclides are very low (Barney and Wood, 1980; Wood and Rai, 1981) and prevent precise determination by conventional chemical analysis. Radiation counting devices are the most sensitive method of measurement of radionuclides in these aqueous samples.

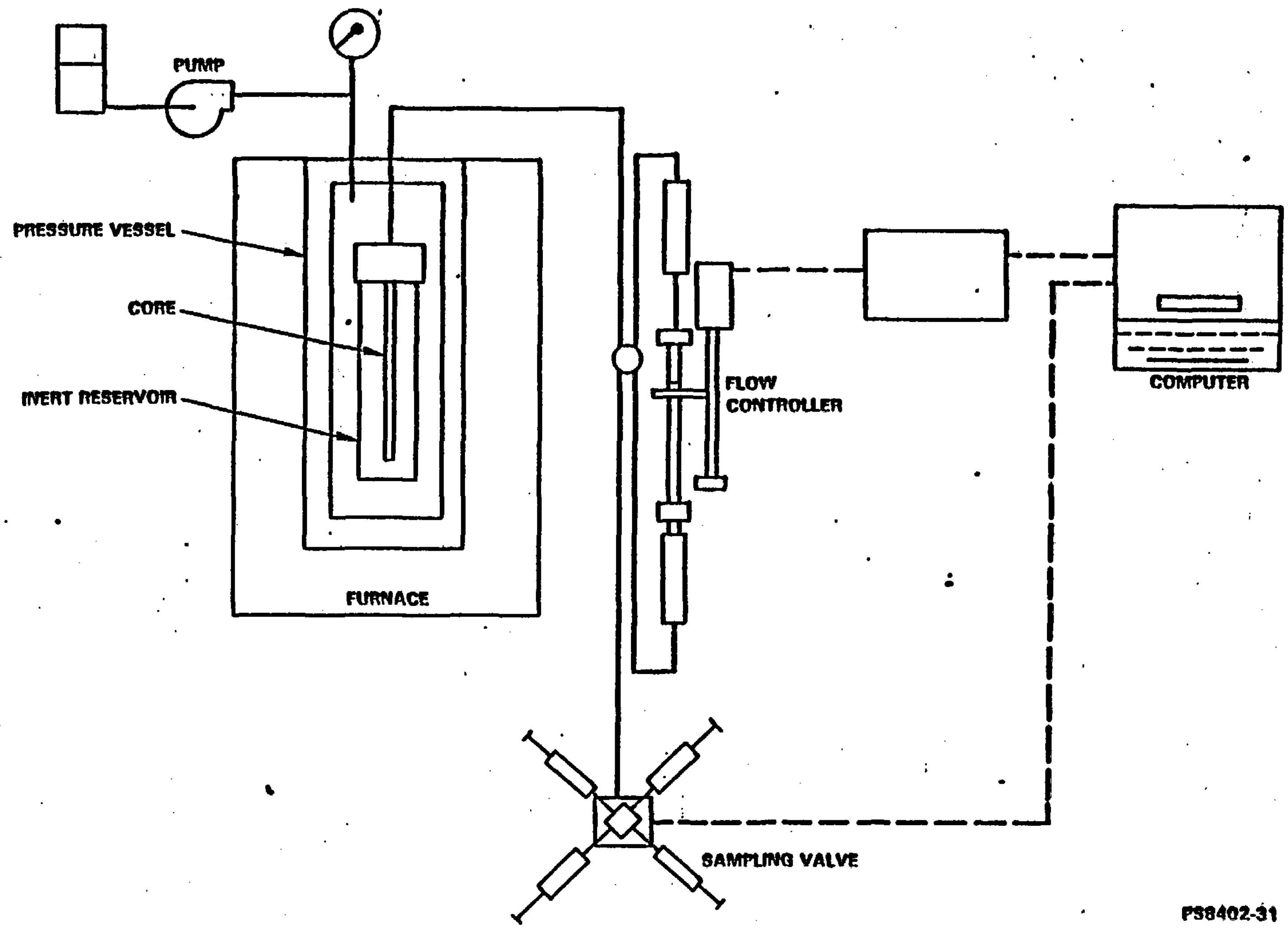


FIGURE D-2. Flowthrough Apparatus.

The required analysis of reacted solids involves both chemical and mineralogical (crystallographic) characterization. Optical microscope, X-ray diffraction, and even scanning electron microscope have some applications to these tasks but are not able to provide analysis on the very small (often less than 1 m) particles of precipitated alteration products that occur in hydrothermal tests. A scanning transmission electron microscope is the only existing instrument that combines quantitative chemical and crystallographic analysis with the necessary spatial resolution. Particulates and colloids suspended in solution may also be an important mechanism for radionuclide migration in groundwaters. Because of the small size of such colloids, typically much less than 1 m or even 0.1 m (Krauskopf, 1979; Champ et al., 1982, Buxton et al., 1982), their isolation by proper filtration techniques is a vital requirement in the hydrothermal testing program.

REFERENCES

Apted, M. J. (1982), "Overview of Hydrothermal Testing of Waste Package Barrier Materials at the Basalt Waste Isolation Project," RHO-BW-SA-228 P, Rockwell Hanford Operations, Richland, Washington, 21 p.

Barney, G. S. and B. J. Wood (1980), "Identification of Key Radionuclides in a Nuclear Waste Repository in Basalt," RHO-BWI-ST-9, Rockwell Hanford Operations, Richland, Washington, 29 p.

Buxton, G. V., T. Rhodes, and R. M. Sellers (1982), "Radiation Induced Dissolution of Colloidal hamatite," Nature, Vol. 295, pp 583-585.

Champ, D. R., W. F. Merritt, and J. L. Young,(1982), "Potential for the Rapid Transport of Plutonium in Groundwater as Demonstrated by Core Column Studies," W. Lutze, Ed., Scientific Basis for Nuclear Waste Management, Vol. V, Elsevier Science Publishing Co., New York, pp.745-754.

Cherry, J. A., A. U. Shaikh, D. E. Tallman, and R. V. Nicholson (1979), "Arsenic Species as an Indicator of Redox Conditions in Groundwater," in W. Back and D. A. Stephenson (Guest Editors), Contemporary Hydrogeology--The George Burke Maxey Memorial Vol. J Hydrology, 43, pp. 373-392.

Danielson, M. J. (1980), Development of the High-Temperature Redox Electrode," PNL-3377, Pacific Northwest Laboratory, Richland, Washington, 41 p.

Dickson, F. W., C. W. Blount, and G. Tunnel (1963) "Use of Hydrothermal Solution Equipment to Determine the Solubility of Anhydrite in Water from 100°C to 275°C and from 1 Bar to 1,000 Bars Pressure," American Journal of Science, 261, pp. 61-78.

DOE-RL (1982), "Site Characterization Report for the Basalt Waste Isolation Project," DOE-RL 82-3, Rockwell Hanford Operations for the U.S. Department of Energy, Washington, D.C., 2,000 p.

Jacobs, G. K. and Apted, M. J. (1981), "Eh and pH Conditions for Groundwater at the Hanford Site, Washington: Implications for Radionuclide Solubility in a Nuclear Waste Repository Located in Basalt," RHO-BWI-SA-174, Rockwell Hanford Operations, Richland, Washington, 1 p.

Krauskopf, K. B. (1979), Introduction to Geochemistry, McGraw-Hill Book Company, New York, New York, 617 p.

MacDonald, D. D. (1978), "Reference Electrodes for High Temperature Aqueous Systems--A Review and Assessment," Corrosion (Houston) 34, pp. 75-84.

MCC (1981), "Materials Characterization Center: Test Methods, Preliminary Version," PNL-3990, Pacific Northwest Laboratory, Richland, Washington, 220 p.

Niedrach, L. (1980), "Oxygen Ion Conducting Ceramics: A New Application in High Temperature High Pressure pH Sensors," Science, 207, pp. 1200-1202.

Seyfried, W. E., Jr. and J. C. Bischoff (1979), "Low Temperature Basalt Alteration by Seawater: An Experimental Study at 70°C and 150°C," Geochim. Cosmochim. Acta, 43, pp. 1937-1947.

Wood, B. J. and Rai, D. (1981), "Nuclear Waste Disposal Actinide Containment in Geologic Repositories," PNL-SA-9549, Pacific Northwest Laboratory, Richland, Washington and RHO-BWI-SA-143, Rockwell Hanford Operations, Richland, Washington, 31 p.

APPENDIX E
REVIEW OF THERMAL GRADIENT EFFECTS ON MASS TRANSPORT UNDER HYDROTHERMAL CONDITIONS

APPENDIX E
REVIEW OF THERMAL GRADIENT EFFECTS ON MASS TRANSPORT UNDER HYDROTHERMAL CONDITIONS

Recent rock/water hydrothermal tests have been performed in a thermal gradient, both under static (Thornton and Seyfried, 1982) and dynamic (Charles and Bayhurst, 1983; Moore et al., 1983) flow conditions. The former study attempts to document affects of thermally driven diffusion (the Soret effect) on mass transfer while the purpose of the latter two studies was to determine the mass transport arising from localized dissolution and precipitation and consequential changes in rock permeability.

A maximum temperature gradient of 3°C to 4°C/cm across a waste package is expected at the peak temperature in a nuclear waste repository in basalt (Altenhofen, 1981). This same heat transfer analysis shows that this gradient decreases rapidly to a value of less than 0.10°C/cm several hundred years after repository closure. The ability to establish such small thermal gradients with existing autoclave technology has not been demonstrated. For example, the minimum thermal gradient obtained in the apparatus of Thornton and Seyfried (1982) was 50°C/cm.

A rough approximation can be made of the relative effect of thermally driven diffusion (Soret effect) and chemically driven diffusion. Lerman (1979) shows that the total mass flux due to the Soret effect (F_T) can be ratioed to the total mass fluid (F_d) due to chemical diffusion as follows:

$$\frac{F_T}{F_D} = \frac{D_s \bar{C} \frac{\Delta T}{\Delta Z}}{D \frac{\Delta C}{\Delta Z}} \tag{E-1}$$

where D is the thermal diffusion coefficient, s is the Soret coefficient, $\frac{\Delta C}{\Delta Z}$ is the chemical concentration gradient of a given solution species, $\bar{C}$ is the mean concentration across the diffusion boundary, and $\frac{\Delta T}{\Delta Z}$ is the thermal gradient. Under initial conditions it is assumed that the concentration of radionuclides far from the waste package is zero. Therefore:

$$\bar{C} = 1/2\ C \tag{E-2}$$

substituting Equation (E-2) into Equation (E-1) and cancelling terms, Equation (E-1) reduces to:

$$\frac{F_T}{F_d} \lesssim 1/2\ S\Delta T \qquad \text{(E-3)}$$

The Soret coefficients for measured dissolved species in water are approximately 10^{-3} deg^{-1} (Lerman, 1979). Taking a maximum temperature difference of 30°C across a 15 cm backfill thickness (Altenhofen, 1981; Anderson, 1982) shows that the thermal diffusion mass flux is less than 2% of the mass flux due to chemical diffusion. Given the uncertainties inherent in chemical diffusion calculations and measurements alone, the Soret effect is judged to be inconsequential to mass transport of radionuclides.

Dynamic flow experiments on rock/water systems under thermal gradients also have achieved a minimum thermal gradient of approximately 50°C/cm (Moore et al., 1983; Charles and Bayhurst, 1983). These tests have demonstrated that mass transport down a thermal gradient can occur under flowing conditions. The inference that mass transport of radionuclides might be enhanced under such conditions would, however, be erroneous. In fact, the results show that although solids may undergo preferential dissolution on the high temperature side of a thermal gradient (i.e., next to the waste form), secondary phases immediately precipitate on the low temperature side as these saturated solutions migrate to lower temperature, and, hence, generally lower saturation limits for dissolved species.

It should be noted that the flow of water through a waste package with backfill is expected to be diffusion-limited (see Section 5.1.4, Table 5-5) and that flow-through tests such as those of Moore et al. (1983) and Charles and Bayhurst (1983) cannot be justified on the basis of replicating expected repository conditions. Even assuming that groundwater flow under a thermal gradient might be a desirable set of conditions to experimentally model, there are serious limitations to be considered. First is that no migration, whether under a thermal gradient or not, can occur in a waste package until saturation of the backill is achieved. The exact time of this process is a complex, and currently undetermined, function of several variables, including rate of return to hydrostatic pressure, groundwater flow rate in the repository horizon, and diffusion of vapor through an unsaturated backfill. In any case, saturation will certainly occur long after the maximum (3°C to 4°C/cm) expected thermal gradient of a waste package in an nuclear waste repository in basalt which occurs less than 10 yr after emplacement of the waste package (Altenhofen, 1981). Furthermore, the actual flux of water into the backfill will lead to a higher rate of heat transfer across the backfill. This effect will cause the expected waste package thermal gradients to be even less than calculated by Altenhofen (1981). The Basalt Waste Isolation Project (BWIP) knows of no data which support the contention that mass transport is significantly increased in flow systems when expected repository temperature gradients are on the order of 0.1°C/cm or less as expected for an nuclear waste repository in basalt 200 yr after closure. Accordingly, the BWIP has adopted the use of constant-temperature hydrothermal reaction apparatuses for all the flowthrough tests on waste/barrier/rock interactions.

REFERENCES

Altenhofen, M. K. (1981), "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, 56 p.

Anderson, W. J. (1982), "Conceptual Design Requirements for Spent Fuel, High Level Waste, and Transuranic Waste Packages," RHO-BW-ST-25 P, Rockwell Hanford Operations, Richland, Washington, 69 p.

Charles, R. W. and G. K. Bayhurst (1983), "Rock-Fluid Interactions In a Temperature Gradient: Biotite Granodiorite + H_2O," Journal of Volcanology and Geothermal Research, 15, pp. 137-166.

Lerman, A. (1979), "Geochemical Processes: Water and Sediment Environments," John Wiley and Sons Inc., New York, New York, pp. 96-100; pp. 98-99.

Moore, D. E., C. A. Marrow, and J. D. Byerlee (1983), "Chemical Reactions Accompanying Fluid Flow Through Granite Held in a Temperature Gradient," Geochimica et Cosmochimica Acta, Vol. 47, pp. 445-453.

Thornton, E. C. and Seyfried, W. E., Jr. (1982), "The Soret Effect: Potential for Thermodiffusional Transport in a Nuclear Waste Repository," Geological Society of American Abstracts with Program, Vol. 14, pp. 631.