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Preliminary Geochemical And Physical Testing Of Materials For Plugging Of Man-Made Accesses To A Repository In Basalt

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Rockwell International

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Richland, WA 99352**

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PRELIMINARY GEOCHEMICAL AND PHYSICAL TESTING OF MATERIALS FOR
PLUGGING OF MAN-MADE ACCESSES TO A REPOSITORY IN BASALT

by

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0 EXECUTIVE SUMMARY

0.1 INTRODUCTION

The objective of the Basalt Waste Isolation Project (BWIP) borehole plugging effort, which is carried out under the direction of Rockwell Hanford Operations (Rockwell) at Richland, Washington, is to locate sites and assess the feasibility for developing a repository for terminal nuclear waste storage at depth in the Columbia River basalts beneath the Hanford Site. As part of this effort, Woodward-Clyde Consultants (WCC) has been contracted by Rockwell to provide a preconceptual design for a plug system in man-made openings (boreholes, shafts, and tunnels excavated during repository construction) that will assure containment of radioactive waste products after closure of the repository. The specific purpose of the plug system will be to prevent the migration of harmful amounts of radioactive waste to the biosphere.

The specific objectives of the physical and geochemical testing effort conducted to date by WCC were to: (1) characterize man-made accesses to a repository in basalt, tabulate available information on physical and chemical parameters, and design considerations that help define the plug environment; (2) modify the selection process that was used to verify the list of preferred candidate plug materials identified during the preliminary Borehole Plugging Materials Selection Process (Taylor and others, ~~1979~~); (3) conduct laboratory investigations on the physical and chemical behavior of candidate materials and present the results of the testing programs; and (4) assess the suitability of the various preferred candidate plug materials that might qualify for further testing and consideration in preconceptual plug design

schemes on the basis of the results of the preliminary geochemical and physical testing programs, the materials selection process, and expected environmental factors (both natural and man-made).

The scope of work for the study conducted to date by WCC included: (1) the characterization of man-made accesses to a repository in basalt; (2) laboratory tests and evaluation of materials to assess their suitability to plug man-made accesses to a repository in basalt; (3) a description of the results of a modified materials selection process and the application of the decision analysis technique used in this program; (4) development of a quality assurance program, program plan and schedule, and work plans; and (5) the preparation of this report.

0.2 CHARACTERIZATION OF THE PLUG ENVIRONMENT AND MAN-MADE ACCESSES

The physical and chemical characteristics of the anticipated plug environment will greatly influence the choice of potential plug materials. The selected plug materials will, in turn, influence the selection of plug placement equipment and will also ultimately determine plug system design. Thus, characterization of the plug environment and man-made accesses to plug seats and the repository are of critical importance. The plug environment includes: (1) the inherent components of the geologic environment at the Hanford Site; (2) the proposed location and depth of the repository; and (3) alteration of the natural environment due to both the excavation of the repository and the storage of radioactive waste.

As an extension of the initial description and characterization of the plug environment presented by Taylor and others (1979), available pertinent data were tabulated in a single table Appendix A, (Table A-I). Any such preliminary, comprehensive tabulation of data is, of course, subject to revision. Many values quoted in Table A-I reflect a limited data base. As subsurface exploration proceeds at the Hanford Site, this data base will be enlarged, and new average values and ranges of values will undoubtedly be established. Many aspects of the geometric parameters included in the table are also preliminary in nature and reflect current thinking on possible overall repository design at the Hanford Site.

0.3 SELECTION OF CANDIDATE PLUG MATERIALS

It was recognized at an early stage of the basalt borehole plugging study that materials to be used in plugs will greatly influence the selection of potential placement equipment and overall plug designs. Thus, the list of preferred candidate materials has a strong impact on the direction of the entire program. The original objective of the materials selection process was to identify candidate materials that (1) have a high probability for successful use in plugs; (2) have a high probability of acceptance based on NRC criteria; and (3) can be used in this and subsequent physical and geochemical testing programs. The selection process should also provide a documented defensible method for the logical selection of a small number of preferred materials for initiating testing programs and preconceptual design schemes. The selection process described in Taylor and others (1979) essentially accomplished several of these objectives. Preferred candidate materials, which are thought to have a high probability for successful use in plugs, were identified by that process. Also, these

preferred materials formed the basis for initiation of physical and geochemical testing and preconceptual plug design.

A review of the original materials selection process presented in Taylor and others (1979) suggested the need for a re-evaluation of the process and the possible need for a new approach; it was decided to extend the work effort in materials selection and to make improvements on the initial selection process. Because the selection of materials for inclusion in preconceptual plug design schemes and testing programs is a decision problem, the review and evaluation of the original screening process indicated that the application of decision analysis would help overcome the drawbacks of the initial selection scheme.

The primary objectives of continued evaluation of the selection process and of the application of decision analysis to the problem were: (1) to correct deficiencies in logic in the original selection schemes; (2) to develop a method that avoids the use of weighting and rating factors and cut-off values; (3) to re-examine the initial comprehensive list of materials with a different approach; and (4) to more completely document the steps of the process (specifically the steps used in the decision analysis).

In general, the approach presented in this report helps to clearly determine and organize those factors which are most significant to the final outcome of the selection process and documents the process in a more complete fashion. Reorganization of function classifications and more complete definition of attributes in this new approach make possible the comparison of materials that will have like applications in plug design while maintaining the capability to discriminate among and rank

them using established criteria. The list of preferred candidate materials developed in the selection process described by Taylor and others (1979) was verified by re-evaluation as described in Chapter 3 of this report. This list was the basis for the physical and geochemical testing programs of preferred candidate materials.

0.4 GEOCHEMICAL TESTING PROGRAM

The primary objectives of the geochemical testing program were: (1) to help define the behavior of candidate plug materials in the plug environment; (2) to provide data on the relative stability and reactivity of candidate plug materials; and (3) to identify the most promising materials for consideration in future studies involving plug system design and advanced testing programs. Even though candidate plug materials are considered to be extremely stable and durable, slow chemical reactions not detected in earlier studies could be cumulative over time and could eventually lead to a loss in plug integrity. The need to make reliable predictions of plug behavior for periods of thousands of years places severe demands on any chemical testing program because long-term experiments may be necessary to obtain sufficiently accurate data on which to base these predictions. The geochemical testing program described here is a series of initial screening tests that were intended to permit an evaluation of the suitability of materials based on their short-term chemical reactivities. These tests determined a lower boundary on the level of reactivity to be expected over the useful life of the plug.

Tests for the geochemical testing program were selected by estimates of environmental conditions to which the plug will ultimately be subjected. Preliminary ranges of temperature, pressure, pH, and ground-water composition have been established; chemical degradation mechanisms for the plug materials were hypothesized; and experiments were designed to detect the potential occurrence of reactions under these postulated environmental conditions. Additional constraints on the selection of test procedures were: (1) the length of time available to do the tests; (2) the anticipated low reactivity of plug materials; and (3) the availability of pressure vessels. The potential alteration mechanisms of plug materials are: (1) chemical reactions between plug materials; (2) chemical reactions between the plug materials and the surrounding rock; (3) chemical reactions between the ground-water and the plug materials (dissolution, selective leaching, solution-mediated phase changes or recrystallization); and (4) pressure-induced phase changes. Tests were conducted under static conditions (no agitation) at 250°C and 150°C under the saturated steam pressure of water at 3.9 MPa and at 250°C at high pressure (34.5 MPa). Stirred tests were conducted at 250°C under saturated steam pressure. These tests were performed at the laboratories of SRI, International in Menlo Park, California, on multiple samples of 39 materials and mixtures of materials selected from the results of previous work.

The original procedures used to select the materials for geochemical testing included chemical stability as a major criterion. Consequently, nearly all of the materials that were tested exhibited only slight reactivities, even at elevated temperature. As expected, the geochemical tests did not show major differences among the materials selected for study.

Therefore, these tests do not rule out any of the candidate materials, and all materials appear to be suitable for further study and potential use in plug designs based on these results. Self-cementing characteristics were observed in stirred basalt samples; this is considered a positive, beneficial result which could enhance its performance in potential plug designs. The cementing action appears to reflect chemical reactions and the growth of new mineral phases in crushed basalt samples. An understanding of the reaction and the ability to promote it under static conditions could result in a replacement of manufactured cements by natural materials capable of self-cementation in plug designs requiring structural support.

0.5 PHYSICAL TESTING PROGRAM

The physical testing program was designed: (1) to help select individual materials and mixtures from the list of preferred candidate materials for further testing and use in preconceptual design schemes to plug boreholes, shafts, and tunnels leading to a repository in basalt; and (2) to provide quantitative experimental data on the thermomechanical response of selected mixtures under simulated repository conditions. Candidate materials for physical testing included natural cohesive and non-cohesive granular earth materials, portland cements, hydrothermal cements, and some standard cement additives. These materials are the same as those tested during the concurrent geochemical testing program.

For the purpose of the physical testing program, mixtures made from the candidate materials are classified into three main generic categories: (1) cementitious mixtures; (2) compacted natural earth materials; and (3) clay slurries. These mixtures

were tested in two phases during this program. During an initial phase of screening tests, all preferred candidate materials and mixtures that fell into one of the three generic categories were examined, and the most promising mixtures were selected for further examination in the subsequent phase of the program -- preliminary tests. During the preliminary tests, specific, promising candidate materials and mixtures (selected by the screening phase) were examined in greater detail.

On the basis of this testing program, concrete, grout, compacted earth materials, and clay slurries are all considered feasible materials for sealing man-made accesses to a repository in basalt. Tests conducted during this study evaluated the permeability and bond strength of miniature plug/basalt (host rock) models at low and high temperatures. These tests indicate that it is possible to design mixtures of candidate plug materials that have permeabilities of less than 10^{-8} cm/sec and will form an acceptable bond strength with the host rock. Other major conclusions are: (1) the addition of finely ground silica flour greatly improves the structural and bond strength of portland cement cured at elevated temperature; it also reduces shrinkage of portland cement mixtures cured at standard temperature; (2) compaction test results for bentonite/sand mixtures indicate that compaction to produce a relatively impervious clayey mixture is feasible by standard compactive methods; (3) significant time is required for a miniature, simulated compacted bentonite/sand plug to hydrate (On the basis of test data, the time required to saturate a 7-m diameter compacted bentonite/sand plug with a clay content of 50 percent may be more than 1,000 years.); (4) consolidation test results for bentonite/sand mixtures with a clay content of 50 percent indicate an expansive behavior in these mixtures for unloading pressures less than 2.2 MPa (These results suggest a

high swelling potential and self-healing properties for plugs composed of these materials; the results also suggest that tight contact between the emplaced plug and basalt (host rock) will be maintained even after cyclic thermal loading); and (5) mud contamination of simulated borehole walls during model testing was found to substantially decrease the bond strength of miniature cement and soil plugs with the basalt (host rock), which strongly suggests that drilling mud should be flushed from boreholes before plugging.

Materials preferred for further testing and use in preconceptual plug design schemes and selected on the basis of the physical testing program results are: (1) portland cement Type V, glaciofluvial sand and gravel, and crushed basalt in various cementitious mixtures and grouts containing an assortment of additives, such as aluminum powder (to promote expansion), a water-reducing retarder agent (to reduce water demand in cements and improve workability), finely ground silica (to reduce shrinkage and improve thermal stability and structural strength at high temperature), and a natural high-silica pozzolan (to reduce shrinkage, increase workability, improve impermeability, and increase stability at low to moderate temperature); (2) Wyoming and Oregon bentonites and glaciofluvial sand in compacted natural earth materials; and (3) processed bentonite, precompacted bentonite pellets, and crushed basalt in clay slurry mixtures.

0.6 SUITABILITY OF MATERIALS FOR USE IN PRECONCEPTUAL PLUG SYSTEMS

Both the physical and geochemical testing programs used essentially the same set of samples prepared from the list of preferred candidate materials. The geochemical program

examined reaction rates of individual materials in simulated ground water (similar to that expected to exist at the depths of plug seats on the Hanford Site) and the reaction rates of mixtures of candidate materials in simulated ground water. The tests were performed under a variety of temperatures and pressures designed to maximize potential reactivity between the various components. The physical testing program combined the candidate plug materials (using various grain size proportions) in mixtures that are precursors to actual plug designs. These tests were, again, designed as a screening step to select those individual materials and mixtures that exhibited the most desirable performance when submitted to a wide variety of mechanical and physical test sequences. On the basis of geochemical testing, all preferred candidate plug materials are considered suitable for further testing and use in preconceptual plug design. Small differences in relative reactivity were noted for the various samples, but the reactivities of all test samples were so low that all test materials are considered acceptable. The self-cementing characteristics of basalt under hydrothermal test conditions give this material an added degree of desirability at this stage of evaluating plug materials. On the basis of the physical testing program, seven preferred material mixtures that were designed and tested during the physical testing program for preconceptual plugging systems were selected as suitable for sealing man-made accesses to a nuclear waste repository in basalt.

The combined results of both testing programs indicate that the materials considered suitable for further testing and use in preconceptual design schemes are various combinations of compacted natural materials, grouts, and concretes. Geochemical testing shows that the materials are generally

non-reactive or have very low reactivities in the hydrothermal test conditions employed during laboratory testing at SRI, which suggests stability in the proposed plug environment. Physical testing indicates that mixtures with the requisite mechanical properties can be designed into plugs from these materials.

0.7 LIMITATIONS OF THE RESULTS

In each of the previous sections, significant steps in establishing design limits and selecting materials for preconceptual plugs and systems are discussed. However, limitations exist on the uses of the data and results presented in this report. Many of the values for physical and chemical parameters presented in Chapter 2 are based on only a limited number of measurements and/or tests. Design conditions (such as borehole diameters, hydraulic gradients, lithostatic stress, etc.) are preliminary in nature and are subject to future revision. Thus, the total characterization of man-made accesses and the plug-seat environment will undergo constant review, and information in this report should be used with these limitations in mind.

It should be noted that the list of preferred candidate plug materials developed by the present selection process is by no means a final selection of materials for all future plug testing and design. The list is not intended to limit the number of materials that can be considered in plug design and testing programs. Materials that have not yet been considered in selection processes and may have potential application in various plug functions could be added in a reprocessing of the initial, comprehensive list of potential materials. Also, the number of material properties used to rank materials may be

expanded, thus requiring modification of the details of the decision analysis performed during this study. Another limitation of the materials selection process is that only materials to be used as major plug components were considered; additives (materials added to plugs in small amounts to produce certain desirable conditions) were not included in the screening. However, the laboratory testing programs have already begun to rectify this last limitation. Various additives (particularly to cements) were investigated as the testing programs proceeded.

The results of the geochemical and physical testing programs represent the first major steps in further examining and screening candidate plug materials. Materials determined as suitable for future testing and preconceptual design work as a result of these testing programs will require detailed examination before final preconceptual design schemes can be adopted. The results of the materials testing programs are used in preliminary, preconceptual design and for the selection of plug placement equipment; subsequent reports will describe this preconceptual design work. Detailed design work will require advanced geochemical and physical laboratory testing, in-situ borehole testing of plug designs, computer modeling of various plug designs and schemes, and the incorporation of many additional physical and chemical parameters in order to refine the selection of materials, machines, and plug designs.

0.8 CONCLUSIONS AND RECOMMENDATIONS

Work recently completed for the engineered barriers effort of the BWIP is described in this report. The primary objectives of the study have been met during this phase of work:

- Man-made accesses to a repository in basalt and details of the plug environment have been characterized. This characterization is in the form of a lengthy tabulation, and known and postulated conditions for these accesses and the environment are referenced;
- The materials selection process developed earlier was reviewed and modified. The modified selection process utilized a recognized decision analysis technique. The list of preferred candidate materials developed by the modified selection process confirmed the general validity of the list of preferred materials developed earlier;
- Geochemical and physical testing programs for evaluating the chemical stability and physical properties of candidate plug materials were completed during this phase of the work and are reported here; and
- The results of the testing programs were used to evaluate the suitability of materials from the preferred candidate list for use in preliminary preconceptual plug designs.

The major conclusions from the work described in this report are:

- The preconceptual plug system design is based on the available data for environmental conditions (both natural and man-made) at the Hanford Site. (Final plug design may require additional data.);
- The results of the geochemical testing program indicated that the candidate plug materials selected are chemically non-reactive during laboratory tests that simulated some

of the expected environmental conditions. Agitated, crushed-basalt samples and mixtures containing basalt were found to be self-cementing under the hydrothermal conditions of the laboratory tests. This ability is considered a positive finding for this material because natural materials that have the capability of self-cementation may replace manufactured cements in some plug applications requiring structural support;

- On the basis of physical test results, those materials considered most suitable for consideration in future test programs and preconceptual plug design are mixtures of natural materials (basalt, clay, glaciofluvial sand, gravel, and zeolite) and processed natural materials (portland cement Type V and grouts plus additives); and
- On the basis of results from both geochemical and physical testing programs, those materials considered most suitable for future test programs and preconceptual plug design are combinations of natural and processed natural materials, most of which are readily available at or near the Hanford Site. Most importantly, all of these materials exhibit chemical stability under conditions that approximate the expected plug environment, and all can be combined and engineered under laboratory conditions to produce mixtures that have low permeabilities and/or requisite structural strength and other behavioral characteristics desirable in preconceptual plug designs.

The following recommendations appear appropriate in view of the above:

- A comprehensive program should be developed for the advanced testing of chemical stability factors critical to the performance of borehole plug materials used in plug systems;
- An advanced physical testing program should be developed which will support repository backfill and borehole plugging needs during field testing, demonstration, licensing, and repository construction;
- Analytical modeling of borehole plug design and systems should be undertaken to serve several functions in the design/construction process;
- A program should be undertaken to evaluate the impact on the design and performance of borehole plugs of natural fractures in basalt flows and the effects of disturbed rock and rock fracturing that may accompany tunnel and shaft excavations and related repository borings;
- A preliminary field test of shallow borehole plugging technique should be performed at the Hanford Site. This field testing should examine leading candidate plug materials and plug placement schemes and should incorporate data and results from the laboratory effort and programs described in the other recommendations above; and
- Additional and more reliable data need to be acquired at the Hanford Site in order to better evaluate plug materials and systems for final selection.

1 INTRODUCTION

1.1 BACKGROUND

In 1976, the U.S. Department of Energy (DOE) established the National Waste Terminal Storage Program (NWTs). The objective of this program is to provide regional nuclear waste storage facilities in various deep geologic formations within the United States. The Office of Waste Isolation (OWI) at Oak Ridge National Laboratory was established to provide program management for the terminal storage program. In 1978, the functions of this office were superseded by the Office of Nuclear Waste Isolation (ONWI) at Battelle in Columbus, Ohio.

The NWTs program includes the investigation of a number of rock types and geologic environments to determine their suitability for terminal storage of radioactive waste. The Columbia River basalts, which underlie a large portion of eastern Washington State and adjacent portions of Oregon and Idaho in the Pacific Northwest, were identified as a possible repository rock. In 1976, Rockwell was given the responsibility of investigating these basalts as a potential site for terminal storage of commercial nuclear waste. Within Rockwell, this study is the BWIP.

In order to construct a subsurface repository in basalt, man-made openings will be required for exploration, access shafts and tunnels, and storage areas. The diameters of these man-made openings, which are collectively referred to as boreholes, may range from 5 cm for existing vertical exploration holes to 6 or 7 m for shafts and tunnels (upper limits of 9 to 10 m are

expected). When the repository is decommissioned, these boreholes will be sealed, or plugged, to preserve the integrity of the repository.

Woodward-Clyde Consultants (WCC) has been contracted by Rockwell to help achieve the objectives of the BWIP. The objective of the WCC study is to devise a plug system (materials, machines, placement techniques, and instrumentation) to seal boreholes, shafts, and tunnels leading to a radioactive waste repository 900 to 1,500 m below the surface of the Columbia Plateau.

The materials and systems (integration of plug materials, plug emplacement machines, and monitoring) selected for the borehole plug must be compatible (stable) with the physical and chemical properties of the surrounding repository rock and its geologic environment. The plug system will be emplaced by machines and techniques that will provide a high degree of confidence in the security and durability of the plugs.

The purpose of the plug system is to prevent the migration of harmful amounts of radioactive waste to the biosphere. To prevent this migration along man-made openings, it is likely that a variety of materials and a series of multiple plug barriers will be used. The materials under consideration include hard rock, portland cement concretes, chemical cements, grouts, clay, sand, gravel, and mixtures of these. Each material or mixture of materials will contribute one or more favorable attributes to complement and preserve the integrity of the repository flow.

The WCC investigation consists of three tasks: Task I (Planning and Procurement); Task II (Testing and Preconceptual Systems); and Task III (Borehole Plugging Field Tests and Preconceptual Design of Plugging Systems). Initial work was completed in fiscal year 1979 and is described in the report "Borehole Plugging of Man-Made Accesses to a Basalt Repository: A Preliminary Study" (Taylor and others, 1979) published by Rockwell as RHO-BWI-C-49. This present report describes a portion of the work completed in fiscal year 1979 - 1980. Subsequent reports will describe the remainder of work completed during this same period.

The objectives of the Task I study included: (1) the preparation of a preliminary list of candidate plug materials; (2) a description of available machinery capable of placing candidate plug materials; and (3) the development of physical and geochemical testing programs to help evaluate the chemical stability and physical properties of candidate plug materials.

The most significant finding from work to date is that, given reasonable regulatory criteria, nothing has been identified which would prevent the design of a plug system to seal man-made openings leading to a nuclear waste repository in Columbia River basalt for significantly long periods of time (on the order of thousands of years). Work accomplished to date indicates that this plug system can be designed using both natural and manufactured materials and can be emplaced with existing placement machinery and modifications of that machinery. Other important findings are:

- Potential candidate plug materials appear to be compatible with the chemical and physical properties of the plug environment;

- These candidate plug materials have characteristics that will tend to sorb or otherwise inhibit the migration of radionuclides;
- Although gaps and uncertainties are present in existing data concerning the plug environment, sufficient information has been identified to initiate preconceptual plug design; and
- Geochemical and physical testing programs can be developed and used to help define potential plug behavior parameters in an initial laboratory simulation of the plug environment.

1.2 SCOPE OF WORK

The fiscal year 1979-1980 work is presented in two parts: preliminary testing of materials for plugging of man-made accesses to a repository in basalt, which is described in this report, and preconceptual systems and equipment for plugging of man-made accesses to a repository in basalt, which is described in a separate report.

The scope of the preliminary materials testing work (described in this report) included the following areas:

- A characterization of man-made accesses to a repository in basalt;
- Laboratory tests and evaluations of materials to assess their suitability to plug man-made accesses to a repository in basalt;

- A description of the results of a modified materials selection process and the application of decision analysis in this process;
- A quality assurance program, program plan and schedule, and work plans; and
- Preparation of a report.

The technical work was initiated by the collection of additional data to characterize boreholes. A geochemical testing program and a physical testing program were conducted to evaluate selected materials and their suitability to plug man-made accesses to a repository in basalt. SRI, International of Menlo Park, California conducted the geochemical testing program as a subcontractor to WCC. The physical testing program was conducted at the WCC laboratory in Oakland, California.

Decision analysis was utilized to review, modify, and supplement the materials selection process. Materials that were utilized in the geochemical and physical testing programs and in the preconceptual plugging schemes, and that were identified as preferred candidate materials by the selection process developed during Task I, were verified by the Task II modified selection process utilizing decision analysis.

Quality assurance and project management are also considered indispensable parts of this project because they provide a mechanism for conducting the program in a logical, traceable, and documented manner. The identification of required procedures, scheduling, and cost control were the elements of quality assurance and project management in this work. Monthly

progress reports were made to Rockwell, and periodic progress meetings were held either at the WCC offices in San Francisco, California, or at the Rockwell offices in Richland, Washington. The progress of the program was also discussed and reviewed at two meetings of the project Technical Review Board, which includes: Mr. Douglas Moorhouse, WCC; Mr. Lloyd Cluff, WCC; Dr. Ulrich Luscher, WCC;; Dr. James Mitchell, University of California, Berkeley; Dr. Konrad Krauskopf, Stanford University; and Mr. Tyman Fikse, Fikse Engineering, Seattle, Washington. The program was also supplemented by telephone conversations between the WCC project manager and the technical liaison for Rockwell.

1.3 ORGANIZATION OF REPORT

The remaining chapters of this report include Chapter 2--a description of the plug environment, Chapter 3--a discussion of the modified process for selecting candidate plug materials, Chapters 4 and 5--descriptions of the geochemical and physical testing programs and the analytical results of those programs, Chapter 6--a discussion of the suitability of preferred candidate plug materials for further testing and consideration in preconceptual plug schemes, Chapter 7--limitations on the results and data of present work, and Chapter 8 -- conclusions and recommendations.

Appendices contain: (1) a detailed tabulation of the characteristics of the plug environment (Appendix A); (2) further discussion of the selection of candidate plug materials (Appendix B); and (3) a tabulation of data and results of the geochemical testing program (Appendix C).

2 CHARACTERIZATION OF THE PLUG ENVIRONMENT AND MAN-MADE ACCESSES

2.1 INTRODUCTION

An essential part of the BWIP (and the primary objective of WCC's participation in the BWIP) is to devise a plug system to seal boreholes, shafts, and tunnels leading to a high-level nuclear waste repository located 900 to 1,500 m deep in a basalt flow of the Columbia River Basalt Group. The physical and chemical characteristics of the plug environment will greatly influence the choice of potential plug materials, which will, in turn, influence the selection of plug placement equipment and will ultimately determine plug system design. Thus, characterization of the plug environment and man-made accesses to plug seat locations and the repository are of critical importance.

The description of the plug environment presented in Chapter 2 and Appendix A of Taylor and others (1979) focused on those aspects of the natural environment (geotectonic, physical, and chemical) that will most likely affect plug design, plug systems, and plug stability. That description was based on a review of available literature, Rockwell reports, relevant reports from other private investigations, drilling logs, core samples, hydrogeologic records, geochemical studies, geologic maps, and lithologic, petrologic, and stratigraphic studies. That review was supplemented by conversations with knowledgeable individuals at Rockwell and various universities, including Stanford, The Pennsylvania State University, and the University of California, Berkeley.

2.2 THE PLUG ENVIRONMENT

The plug environment includes: (1) the natural components of the geologic environment at the Hanford Site; (2) the proposed location and depth of the repository; and (3) alteration of the natural environment due to both the excavation of the repository and the storage of radioactive waste. Conditions important to borehole plugging include the chemistry, mineralogy, and petrology of the host rock; rock strength of basalt; bedding attitudes; the position of aquifers; permeabilities of flows and interflow units; lithostatic pressure; potential maximum hydrostatic pressure; regional subsidence and related stresses; the parameters of potential earthquakes; general joint and fracture patterns within flows (flow top, entablature, and colonnade); temperature of the host rock; geochemistry of the ground water; and secondary minerals filling basalt fractures, joints, and other natural openings.

Some characteristics of the plug environment will be greatly influenced by the excavation of tunnels, shafts, and the repository itself and by placement of spent fuel, backfill, plugs, and other engineered barrier components. These characteristics are dependent on the design of the repository and the plug system and can only be discussed in terms of potential configurations of the system and the repository. For example, relief of accumulated stress during excavation, or the accumulation of stress following plugging, may conceivably affect the integrity of the repository by either inducing new fractures or opening existing fractures within the repository flow, thus increasing the permeability of the rock mass. The orientation of the repository and plugs, existing fracture orientations, and induced fractures may be influenced by the

magnitude and orientation of the stress field. Permeabilities of various units within the plug environment may be increased or decreased by excavation methods or injection grouting.

Previous work indicated the strong need for a tabulation of all environmental conditions that might affect the selection of plug materials and the preconceptual plug design. Such a tabulation would provide workers within WCC and Rockwell with a common source of accepted, current values for a host of environmental conditions. In addition, by listing the many conditions, definition of the total environment at plug seats could be initiated, and workers would be able to more readily detect and address deficiencies in currently available data. Thus, as an extension of the initial description and characterization of the plug environment, available pertinent data were tabulated in a single document and appropriately referenced. This tabulation is presented in Table A-I of Appendix A, located at the back of this report.

2.3 TABULATION PROCEDURE

Table A-I in Appendix A was an outgrowth of the documentation of parameters presented throughout Taylor and others (1979), particularly Chapter 2 and Appendix A. These data and other information collected during the present study and relating to the natural environment and projected changes to this environment are included in Table A-I. In addition, available data on the anticipated geometry of man-made accesses (hole diameters, depth, etc.) to be superimposed on the natural environment are also included in Table A-I. Multiple data sets are available for many of the values quoted for chemical and physical parameters. Where appropriate, multiple values for the same parameters have been listed in Table A-II of

Appendix A and have been completely referenced. The introduction to Appendix A describes the method used to select a value or range of values included in Table A-I for cases where multiple measurements are listed in Table A-II.

Data in Table A-I are tabulated with respect to four postulated borehole sub-environments: vertical boreholes that start at the surface; horizontal boreholes that start in the subsurface; tunnels; and shafts. Many additional environmental parameters were added and quantified where possible during the preparation of Tables A-I and A-II.

2.4 DISCUSSION

Any such preliminary, comprehensive tabulation of data is, of course, subject to revision. Many values quoted in Table A-I reflect a limited data base. As subsurface exploration proceeds at the Hanford Site, this data base will be enlarged, and new average values and ranges of values will undoubtedly be established. Many aspects of the geometric parameters included in the table are also preliminary in nature and reflect the most current thinking on possible overall repository design at the Hanford Site.

In spite of its preliminary nature, Table A-I has already proven very useful. It is the source for defining some of the attribute scales assigned to properties that are used in ranking materials during the materials selection process described in Chapter 3 and Appendix B of this report. Table A-I also lists many of the assumed preconceptual design conditions that were applied to the initial plug system designs and machinery selection schemes developed during this study.

3 SELECTION OF CANDIDATE PLUG MATERIALS

3.1 INTRODUCTION

A preliminary scheme for selecting candidate plug materials for man-made accesses at the Hanford Site was presented in Chapter 3 and Appendix B of Taylor and others (1979). It was recognized at an early stage of this study that materials to be used in plugs will greatly influence the selection of potential placement equipment and overall plug designs. Thus, the list of preferred candidate materials has a strong impact on the direction of the entire program.

A review of the original selection process presented in Taylor and others (1979) suggested the need for a re-evaluation of the materials selection process and the possible need for a new approach. This review indicated that in the preliminary scheme: (1) the scales of several evaluation measures were not completely defined; (2) a rationale was not presented for the evaluation measures that were used; (3) the use of weighting and rating factors and of specific cut-off values in various screens was not explained; and (4) the organization and use of the successive screens were not explained. In addition, the ranking of the materials examined during this initial selection process was found to be highly sensitive to some of these factors (particularly to the use of rating and weighting values and the relative organization of the screens used in the process).

It was decided to extend the work effort in materials selection and make improvements on the initial selection process during this study. Because the selection of materials for inclusion in a preconceptual design and testing program is a decision

problem, the selection process can be appropriately viewed as a decision analysis. The concept of dominance in decision analysis (also referred to as efficiency) used in this modified materials selection process dates back to the classic work of Pareto (1897) on welfare economics. This work has been utilized successfully in a variety of evaluation problems involving multiple attributes (for example, Ford and others, 1979; Keeney, 1973). The interested reader is referred to Holloway (1979) for an elementary discussion of dominance, or Keeney and Raiffa (1976) for a more advanced presentation. Other relevant work is presented in Zeleny (1973).

Within a formal decision analysis, the following four steps need to be carried out:

- Structuring the problem: includes determining what objectives are being pursued, what alternatives might potentially meet those objectives, and what the constraints on the problem are;
- Determining the evaluation (utility) function: includes determining what evaluation measures (attributes) will be used to measure how well each objective is met and determining how the various attributes will be combined to arrive at a single overall measure of the desirability of each alternative;
- Estimating attribute levels: includes an estimation, based on data or expert judgment, of the level of each attribute that each alternative will achieve. If appropriate, a quantification of uncertainties in these estimates is made; and

- Evaluation of alternatives: includes an integration of the results of the previous steps to evaluate the relative desirability of each alternative. In some situations there are disagreements about the estimated attribute levels or the evaluation function. In such cases, a sensitivity analysis is conducted to determine how these disagreements affect the evaluation results.

The review and evaluation of the original screening process indicated that the application of decision analysis would help overcome the drawbacks of the initial selection scheme discussed above.

The remainder of this chapter briefly reviews (1) the development and rationale of the modified materials selection process, and (2) the application of the process to select a list of preferred candidate plug materials for use in preconceptual design and testing. This list (Table I) verifies the results of the original selection process (Taylor and others, 1979). (See Chapter 3 and Appendix B of Taylor and others [1979] for a complete description of the original selection process.) Additional details of the modified process developed during the present study are presented in Appendix B of this report.

3.2 DEVELOPMENT AND RATIONALE FOR THE MATERIALS SELECTION PROCESS

3.2.1 General Objectives of the Process

The original objectives of the selection process were to identify candidate materials that: (1) have a high probability for successful use in plugs; (2) have a high probability of

TABLE I

PREFERRED CANDIDATE PLUG MATERIALS*

<u>Material</u>	<u>Desirable Attributes</u>
Basalt	Relatively impermeable as a solid plug Good strength for engineering purposes Low (but some) ion exchange potential and moderate sorption capacity Low cost, high availability
Quartz (only as a solid plug for small boreholes)	Impermeable Good strength Chemically stable Low cost
Smectite clays	Very impermeable High ion exchange potential and sorption capacity Chemically stable Low cost, readily available
Clinoptilolite	High ion exchange potential and sorption capacity Chemically stable Low cost, readily available
Steatite (only as a solid plug for small boreholes)	Low permeability Good strength Low cost
Grouts portland cements hydrothermal cements	Low permeability High adaptability Low cost, readily available
Concretes portland cements and aggregate hydrothermal cements and aggregate	Good strength Low permeability High adaptability Low cost, readily available
<hr/> *Selected by the modified materials selection process described in this report.	

acceptance based on U.S. Nuclear Regulatory Commission (NRC) criteria; and (3) can be used in the physical and geochemical testing programs. The selection process should also provide a documented defensible method for logically arriving at a small number of preferred materials for initiating testing programs and preconceptual design schemes. The most promising plug materials from a vast array of potential candidates were selected at an early stage in the development of the program. Because many methods of selection are possible, one important objective was to clearly document the rationale underlying the selection process used in this study.

The selection process described in Taylor and others (1979) essentially accomplished several of these objectives. Preferred candidate materials, which are thought to have a high probability for successful use in plugs, were identified by that process. Also, these preferred materials formed the basis for initiation of physical and geochemical testing and preconceptual plug design.

The primary objectives of continued evaluation of the selection process and of the application of decision analysis to the problem are: (1) to correct deficiencies in logic in the original selection scheme; (2) to develop a method that avoids the use of weighting and rating factors and cut-off values; (3) to re-examine the initial comprehensive list of materials with a different approach; (4) to more completely document the steps of the process (specifically the steps used in the decision analysis); and (5) to develop an analytical approach that can be generalized and applied to materials selection problems pertaining to backfill and canister hole plugs. Thus, the re-evaluation of the original materials selection process

and the application of a decision analysis to materials selection made possible the attainment of all objectives discussed above.

3.2.2 Structure and Objectives of the Decision Analysis

As discussed above, the modified selection process is a decision analysis, and therefore, the four steps of a decision analysis outlined in Section 3.1 must be addressed.

3.2.2.1 Structuring the Problem

The constraints on the selection of materials are substantial because a plugging system must maintain its functional capabilities for thousands of years without human intervention. In addition, this study was restricted to considering materials which do not require the collection of substantial amounts of new data.

These considerations resulted in the following objectives for the materials selection process:

- Selected materials must be compatible with the natural environment expected in the repository shafts, tunnels, and boreholes;
- Selected materials must have a documented history of survival for a period of time on the order of that expected for the containment lifetime of the repository;
- Selected materials must be sufficiently documented so that relevant physical and chemical properties can be specified;

- Selected materials should provide, in a superior manner, at least one of the three functions (inhibit fluid flow, inhibit radionuclide migration, or provide structural integrity, as discussed in Section 3.3.3) needed in a plugging system; and
- Selected materials should be practical to use. This requires consideration of a variety of concerns, including cost, availability, ease of placement, etc.

Note that the first three objectives must be met by any selected material. If either of the first two objectives are not met by a material, conservative engineering practice dictates that the material not be used. If the third objective is not met, consideration of the material is outside the scope of the study. The last two objectives differ from the first three in that materials might meet these objectives to differing degrees and still be acceptable as potential plug materials.

3.2.2.2 Determining Evaluation Functions

In choosing appropriate material properties for measuring how well a material meets the fourth objective listed above, it is necessary to keep in mind that materials will be evaluated with respect to three different potential functions in plugs. Obviously, the properties used to measure how well materials inhibit fluid flow are different than those used to measure how well they provide structural integrity.

Multiple properties are needed to completely assess the ability of a material to perform one of these functions, and all of these properties are considered together when evaluating the

overall ability of a material to perform one of the functions. Because the relative importance of the various properties will depend to some extent on details of plug system design (not yet determined), specific statements of a property's relative importance are avoided as much as possible when carrying out the evaluation.

3.2.2.3 Estimating Attribute Levels

One step in the process is to evaluate the numerical ranges of values quoted in the literature (or from other sources) for the material properties being used in the evaluation. These ranges of values are then broken into attribute scales by assigning numerical attribute levels to incremental parts of the range of values. Because much variation exists for the reported values of many properties of materials under consideration, the range of values quoted for properties is summarized in fairly broad categories in the attribute scales rather than in specific, exact levels. Attribute levels are then determined for a specific material based on the numerical levels in the attribute scales (which represent ranges of values quoted for the material properties) and information on published values for the properties of that material. This step is discussed in detail in Section 3.3.5.

3.2.2.4 Evaluating Alternatives

The first four objectives listed in Section 3.2.2.1 are qualitatively different and are considered to be more significant than the last objective (which is that materials should be practical to use). There are two reasons for this: (1) it is difficult to judge now what will become "practical" over the 50 to 100 years that are likely to elapse before a

repository in basalt is permanently sealed; and (2) "practicality" is very relative. In some people's views, large scale use of nuclear power cannot occur until the terminal waste isolation problem is solved, and without such use of nuclear power there may be severe dislocations in the economy of the United States. If the latter is correct, cost and availability become secondary factors in selecting candidate plug materials.

For this reason, the overall evaluation of a material in the modified selection process has three sequential parts:

- Assurance that the three mandatory objectives are met;
- Determination of how well the physical and chemical properties suit the capability of a material to carry out one or more of the three plug functions (discussed earlier); and
- Qualitative consideration of the various practicality issues to determine whether these issues have sufficient importance to alter the evaluation based only on physical and chemical properties (carried out under the second part above).

In this three-part process, the initial evaluation of the desirability of a material is based only on physical and chemical properties. Thus, if anyone should disagree with the assessment as to what is "practical", he would still be able to use much of the analysis.

3.3 THE MATERIALS SELECTION PROCESS

The considerations discussed in Sections 3.1 and 3.2 led to the development of a seven-step materials selection process during this study. This process is outlined in Figure 1, and the relationship of these seven steps to the four steps of a formal decision analysis (discussed in Section 3.2.2) is illustrated in Table II. A detailed explanation of the selection process discussed in this chapter is presented in Appendix B.

3.3.1 Development of an Initial List of Materials (Step 1)

The initial list of materials (Taylor and others, 1979); to be considered in the modified selection process was assembled by WCC personnel.* This list was reviewed by Dr. Hans Ewoldsen, Project Director, and Mr. Charles Taylor, Project Manager. In assembling any such list, a vast array of potential plug materials could be included. The list used in Taylor and others (1979), which is not exhaustive, reflects the professional judgment of the authors. Obviously, another group of scientists might develop a somewhat different, specific group of materials. However, several guidelines were used in assembling the initial list, and adherence to them by other professionals should produce a similar list:

- Materials included on the list are considered to be potential major plug components. Additives (materials present in plugs in small amounts to serve specific functions) were not included in this screening process;

* Dr. Gary Anttonen and Messrs. Marvin Niccum, Jack O'Rourke and Marc McGovern.

FIGURE 1
MATERIAL SELECTION PROCESS

TABLE II

DECISION ANALYSIS AND THE SELECTION OF CANDIDATE PLUG MATERIALS

Step in the Modified Selection Process for Materials	Equivalent Step(s) in Formal Decision Analysis	Discussion
(1) Development of an Initial List	Structuring the Problem	It is necessary to decide on an initial list of materials from the many thousands that might potentially meet the selection process objectives (Section 3.3.1).*
(2) Preliminary Screening	Structuring the Problem	Materials are evaluated to see if they meet two primary objectives--compatibility with the natural environment and a documented history of survival (Section 3.3.2).*
(3) Function Classification	Structuring the Problem	Materials are classified by function--inhibiting fluid flow, inhibiting radionuclide migration, or providing structural integrity (Section 3.3.3).*
(4) Data Availability Screening	Structuring the Problem	Materials are evaluated to see if they meet a third objective--data availability (Section 3.3.4).*
(5) Determination of Material Properties	Estimating Attribute Levels	Relevant material properties are determined for all materials that meet the above objectives, and numerical attribute levels are assigned after determining attribute scales (Section 3.3.5).*
(6) Evaluation of Physical and Chemical Properties of Materials	Determining Evaluation (Utility) Function and Evaluation of Alternatives	The various attributes used to measure the physical and chemical properties of materials are combined to determine the overall suitability of a material for carrying out a plug function (Section 3.3.6).*
(7) Consideration of Other Factors	Evaluation of Alternatives	The degree to which a material is practical to use (based on cost, availability, and other factors) is evaluated in this step (Section 3.3.7).*

*Reference is to the chapter section where the step is discussed in detail.

- The list is, in part, a sampling of material types rather than a complete list of every conceivable candidate material under a given classification;
- In general, the materials should appear to be compatible with the natural geologic environment at repository depths and with projected changes in this environment produced by drilling boreholes and excavating shafts and tunnels. Some history of a material's use in engineering applications and investigations was also considered desirable;
- The list of materials is based on desirable physical and chemical properties a material may potentially bring to a plug design; and
- Cost and availability of a given material were not considered when the list was assembled.

With respect to the first guideline, note that additives are best evaluated once major plug components, design, and environmental parameters are better known. Each additive can then be assessed on an individual basis with respect to the specific function it might serve. The screening process discussed in Taylor and others (1979), and the modified one described in this chapter and in Appendix B, evaluate the relative desirability of potential major plug components using a set of evaluation measures (attributes). These attributes are applied to the entire list in a sequential manner in order to eliminate less desirable candidates and eventually produce a preferred list of materials. Materials on the list are evaluated individually with respect to their chemical and physical properties. They are not considered in mixtures

during the screening process because the number of possible permutations and combinations is too large. The range of attribute values of chemical and physical properties for mixtures would also become too large.

With respect to the second guideline, the authors used their professional experience and judgment to make the list an appropriate sampling of material types. For instance, various natural materials on the list, such as the zeolite, clinoptilolite, or the crystalline rock (granite), are representative of groups of minerals or rocks possessing particular properties. Likewise, manufactured items, such as concretes, are representative of a class of man-made materials that include many alternate choices. Various factors, such as availability and cost, may ultimately make an alternate possibility in any classification more desirable than the specific one currently listed. However, listing representatives from these groups and comparing their characteristics in the screening process suffices to discriminate between their relative desirability at the present time and at the present level of study and plug design.

The third and fourth guidelines used in assembling the list are considered in more detail during the screening process itself because the range of values for many material properties used in the process reflects both the natural environment at the Hanford Site and the projected changes to that environment produced by excavation of the repository. However, in assembling the initial list, these guidelines generally helped eliminate obviously incompatible or non-durable materials from the list.

The fifth guideline eliminated cost and availability as factors in assembling the initial list. These two factors are treated in a final step of the screening process itself to help distinguish the relative desirability of the most preferred candidate materials. The importance of designing successful plugs and the importance of the physical and chemical properties of materials used in plug construction outweigh economic considerations at this early stage of the materials selection process. Because creation of the initial list is the first step in the process, a comprehensive list of potentially desirable candidate plug materials that are listed without deference to cost and availability was considered essential. As a result, some rare and costly materials (especially precious metals), having potentially desirable physical and chemical properties, appeared on the initial list. Application of the cost factor to all materials at the same point later in the selection process will eliminate certain costly materials. However, for the sake of a uniform application of logic during the process, all materials on the initial list were screened in the same way.

The initial list of candidate plug materials used by Taylor and others (1979) was reviewed during the present study and was found to be generally satisfactory. This list, with the elimination of some materials that were reclassified upon detailed re-evaluation as additives rather than potential major plug components, and with other minor modifications, was used as the initial list (Appendix B, Table B-I) for the analysis described in this chapter.

3.3.2 Preliminary Screening (Step 2)

The original materials selection process described in Taylor and others (1979) was found to be highly sensitive to several major factors. In the original selection process, one of these factors, chemical stability, was incorporated into the general weighting and rating scheme used in that process. In the current approach, these major factors are consolidated into an initial screening procedure that eliminates materials found to be unacceptable on the basis of one or both of the following criteria:

- The material is chemically unstable in the repository environment with respect to expected pH and Eh conditions; and/or
- The material has an insufficiently documented history of survival to assure its stability for periods on the order of thousands of years.

This screen assesses the fundamental chemical compatibility of materials with the repository and geologic environment. It also assesses their documented history of survival through time and their ultimate acceptability as plug materials in plugs that must demonstrate, to a high degree of assurance, their capability for lasting thousands of years. The latter constraint greatly diminishes the acceptability of many man-made materials.

3.3.3 Function Classification (Step 3)

In Step 3, the remaining materials are classified by three major functions: (1) to inhibit fluid flow; (2) to inhibit

radionuclide migration; and (3) to provide structural integrity. Materials that can serve more than one function are classified under all relevant categories. Note that the function classification used here is different from that defined by Taylor and others (1979), which separates materials into potential major plug components and additives. In the current selection process, only potential major plug components are considered. Additives are not included in this process because the objective is to select candidate materials for testing that are potential major components for preconceptual plug designs. Additives will be present only in small amounts and will be tailored to highly specific conditions; they will fulfill a separate, special function and are best evaluated at a later date after major plug components, design, and environmental parameters are better known.

The function classification is necessary because the evaluation process must be somewhat different for each class of materials. In particular, the relevant material properties that need to be considered during evaluation of a material depend on the function for which the material will be used. For example, the ion exchange potential of a material is not important if the material is to be used to inhibit fluid flow; however, if its function is to inhibit radionuclide migration, then ion exchange potential is very important.

This classification of materials anticipates plug design to some extent because materials are categorized according to their projected ability to perform a certain function in the plug. However, such a classification at this stage in the selection process overcomes a major problem of the original screening process developed in Taylor and others (1979). In that process, the relative merits and properties of materials

that are to serve fundamentally different functions in a plug had to be compared in a series of complex screens. As a result, the serious problem of comparing "apples" with "oranges" was greatly increased.

Classification of materials according to the three functions outlined in this section, and the evaluation of each group separately under each classification, enable the selection of properties that measure the performance of a material with respect to a specific function. Thus, materials can be ranked under each classification in accordance with their ability to perform that function as defined by a list of properties relevant to that function. In general, like quantities are being compared by the process.

3.3.4 Data Availability Screening (Step 4)

This screen is individually applied to data available for the various attributes used to rank materials in each function classification in Step 5 (described in the next section). Materials for which large data bases have been accumulated are more predictable than materials for which fewer data are available. It was not within the scope of the present study to expand the data base with respect to specific properties of materials listed under each of the three function classifications. This would require new research and laboratory experimentation for those materials whose physical and chemical properties are little known.

The data availability screen eliminates materials for which data are judged inadequate. University and company libraries, textbooks, scientific journals, and professional reports were consulted to evaluate their relevant properties within the time

constraints of the testing program. For a material to pass this screen does not require that every property discussed under each function classification in the next step (Section 3.3.5) be completely defined in the literature. Materials that are similar to other well-documented materials, or materials that have properties that are well-documented and similar to those discussed in the next section, are considered as having sufficient available information for assigning attribute values on the basis of professional judgment or analogy (as discussed in Section 3.3.5.4). However, those materials that lack sufficient pertinent data on properties of concern (see Section 3.3.5) or lack well-documented analogs are eliminated by this screen.

Obviously, as new data become available, the evaluation produced by this screen may change. It should be re-emphasized that the evaluation is made with respect to data considered pertinent to the basalt borehole plugging problem and to material properties (discussed in the Section 3.3.5). Thus, some materials (particularly man-made ones) are eliminated even though they have relatively large, but inappropriate, data bases with respect to their known properties.

3.3.5 Determination of Material Properties (Step 5)

A wide variety of chemical and physical properties are potentially relevant for evaluating the desirability of a material for use in borehole, shaft, or tunnel plugs. Selecting the appropriate material properties requires that the primary purpose of the materials selection process (i.e., to select materials for inclusion in programs of continued evaluation and testing) be kept clearly in mind. The present objective is not to define the large number of properties for

each material, as will be required in the selection of final designs for plugs. Many properties of a material will be important in deciding on a specific plug design that best utilizes that material. However, during the initial evaluation of whether a material should be considered for use in a plug, only a few critical material properties that will be important regardless of the exact design of the plug should be considered. The following questions were pertinent in developing the procedures used in Steps 5 and 6:

- What material properties should be considered?
- What attributes (evaluation measures) should be used to measure each important material property?
- How should the attribute levels be determined for each material property?
- How should the different attributes be combined to arrive at a single overall evaluation of the chemical and physical properties of each material?

The first three questions are addressed below; the fourth is discussed in Section 3.3.6.

The number and type of material properties considered should be limited to those that will fundamentally characterize the suitability of materials under each function classification. The list of selected material properties under each classification is based on parameters for which adequate data exist in the literature and for which the material's impact on potential plug design can be directly evaluated. Ambiguity surrounds the impact of certain properties on the final

performance of a plug. These properties were not used in the evaluation of materials under each function classification.

3.3.5.1 Properties of Materials to Inhibit Fluid Flow

Permeability is the primary measure of the ability of a material to inhibit fluid flow. Many factors affect permeability, and a range of values for permeability is commonly cited in the literature for any given material. In addition, other physical properties of a material can directly affect the bulk permeability of a plug. One of these, thermal expansion, is included on the list of properties used to evaluate the ability of a material to inhibit fluid flow. Materials with coefficients of thermal expansion similar to that of basalt are more suitable for plugs than materials that have greatly different coefficients of thermal expansion. Separation at the plug/wall rock interface and induced fracturing of the plug or basalt should be less likely to occur during the heating and cooling cycles of the containment period of a repository where the plug has a coefficient of thermal expansion similar to that of basalt. Fracturing induced by materials having thermal expansion coefficients greatly different from basalt could drastically and adversely affect the bulk permeability of the plugs.

Other potentially relevant factors, such as modulus of elasticity and plasticity index, were considered for use as evaluation measures, but the significance of these factors is difficult to determine unless a specific plug design is being evaluated. For instance, high elasticity could either be detrimental or beneficial in a plug material, depending on the plug's proposed use. Both properties could influence the long-term ability of a plug to restrict fluid flow; however, because

the impacts of these factors are unclear (high plasticity, for example, may be desirable in some plug designs to maintain impermeability and undesirable in others), they are not used to evaluate and rank materials. These factors, of course, will be considered once actual plug design is underway.

The two selected factors (permeability and thermal expansion) along with chemical stability assessed in Step 2 (pH and Eh compatibility with the environment), are the bases for determining the overall potential of a material for inhibiting fluid flow in this evaluation.

3.3.5.2 Properties of Materials to Inhibit Radionuclide Migration

Under this function classification, the suitability of those materials which will inhibit the migration of radionuclides (although not necessarily a fluid containing them) was evaluated. In addition to low permeability, a large capacity to exchange ions with the environment is the most important mechanism by which plug material can help control the migration of radionuclides in solution; ion exchange potential and sorption capacity are two primary indicators of this ability.

Ion exchange potential is a measure of the ability of a material to set free and replace ions in its structure with ions in solution in contact with the material. Materials with high ion exchange potentials may have the capacity for setting free ions from their lattice structure and replacing them with (and thus immobilizing) migrating radionuclides.

Sorption capacity is a measure of the general ability of a material to entrap ions migrating in solution; the actual

sorption mechanism for any given material can reflect several phenomena, including van der Waals bonding, the filling of vacant lattice spaces in crystal structure, the entrapment of ions by the host due to unsatisfied bonds along crystal edges (edge effects), as well as actual ion exchange (as described above). Generally, the distribution coefficient (K_d value), which gives a relative measure of the sorption capacity of a material, is a collective, somewhat qualitative assessment of these various phenomena.

Both ion exchange potential and sorption capacity are temperature dependent; for most materials, these factors decrease with increasing temperature. However, thermal stability is not included as a third attribute under this function classification because the temperature at plug seats is expected to be less than 100°C (see Table A-I, Appendix A). Within this expected temperature range, the ion exchange potentials and sorption capacities for most materials are not greatly affected, and thermally induced changes in their properties that might affect ion exchange potential or sorption capacity are expected to be minor. Chemical changes could also adversely alter the ability of a material to block migrating radionuclides. (Step 2 eliminated materials that are chemically unstable in the anticipated environment).

Chemical precipitation, another possible mechanism for inhibiting radionuclide migration, was also considered. However, in general, materials that have the ability to precipitate migrating radionuclides and to form stable mineral products are not candidates as major plug components. They would be present in plugs in small amounts as additives and, therefore, are not considered in this selection process. Thus, ion exchange potential and sorption capacity, in conjunction

with chemical stability (evaluated in Step 2 of the selection process), are the basis for determining the overall ability of a material for inhibiting radionuclide migration in this evaluation.

3.3.5.3 Properties of Materials to Provide Structural Integrity

Structural integrity of the plug will be provided primarily by its ability to resist or accommodate deformation over time. Because materials that provide other important functions of inhibiting fluid flow and radionuclide migration may be rather easily deformed, it is necessary to separately evaluate materials suitable for providing the plug with requisite structural integrity during the containment period of the repository. While deformable, plastic materials will provide some physical continuity, engineering practice indicates that in large openings (shafts and tunnels) such materials will need to be buttressed by more rigid plug components capable of transmitting the various loads that may be imposed on large plugs. Thus, the factors for evaluating the ability of a material to provide structural integrity include strength (in unconfined compression), creep (as a measure of a material's long-term behavior), and its coefficient of thermal expansion. The last factor measures the compatibility of the candidate plug material with host rock and the natural environment. Materials that have thermal expansion properties similar to basalt are preferred. Again, note that chemical compatibility with the environment is evaluated during Step 2 of this selection process.

Other properties that might help measure a material's ability to provide structural integrity (such as consolidation,

compressibility, plasticity, and elasticity) are, in part, design dependent. Under differing circumstances, high or low values of each may be desirable or undesirable. Thus, these properties can not be used in the present phase of materials selection.

3.3.5.4 Determination of Attribute Levels

In order to determine and record material properties in a consistent and easily understandable way, numerical evaluation measures (attributes) are used to summarize the properties of each material. The numerical ranges assigned to the various attribute scales are based on actual data from the natural environment at projected repository depths (e.g., the attribute scale for permeability) or are scaled from published data (e.g., the attribute scale for ion exchange potential).

Assignment of attribute levels to the properties of materials on each list of the three function classifications is made primarily on the basis of published data. Because each level of the attribute scale for each material property was bracketed by a rather broad range of values, uncertainty as to the appropriate attribute levels for particular materials is minimized. In most cases, ranges in published data for the properties of a given material fall within the range of a single defined level for each attribute scale.

Not every property listed as an attribute has been measured for every material (or the pertinent data could not be located in the available time); where necessary, attribute levels are assigned on the bases of analogy with similar materials for which data are available. In other cases, attribute levels were assigned on the basis of judgment and the expected

behavior of a given material. The primary objective of the materials selection process is to select promising materials for future study, and judgmental assignments of attribute levels are accurate enough to meet this objective and still allow comparisons with attribute levels assigned on the basis of data collected from the literature.

3.3.6 Evaluation of Physical and Chemical Properties of Materials (Step 6)

In order to evaluate the physical and chemical properties of materials under each function classification, all attributes of the material are considered together in Step 6. To the extent possible, the desirability of candidate plug materials would be evaluated without assigning specific relative importance to each of the various attributes. This procedure is desirable because the importance of the different factors depends in part on features of plug design that have not yet been determined. For example, the importance that should be attached to having high ion exchange capacity depends on the degree to which this mechanism will be used to trap radionuclides in the plug. This has not yet been determined. In addition, the approach used herein avoids the weighting factors and cut-off values applied in the original selection process described in Taylor and others (1979).

The evaluation procedure used here is dominance analysis, which does not require any assignment of relative importance to the various properties. Appendix B, Section B.7, describes in detail the application of dominance analysis to the current materials selection process; this application resulted in a list of materials ranked from most to least preferred in each function classification. This list categorizes materials by

the relative desirability of their physical and chemical properties. However, all materials in each function classification are not precisely rank-ordered for two reasons: (1) because each attribute scale has only a few different levels, several materials have the same levels for all attributes. Thus, these materials will always rank the same, regardless of what procedure is used to combine the various attributes; and (2) because only dominance concepts are used in the evaluation and no statements are made about the exact relative importance of the various material properties, the decision of which of any two materials in question has the most desirable physical and chemical properties is not always possible.

In most cases, the first of these two reasons resulted in materials being ranked as equally preferable. There are only two situations in the set of three lists (one for each of two function classifications) for which additional information about the relative importance of attributes could lead to a more detailed ranking of the materials. Both of these situations involve materials that are ranked relatively low, and hence, a more detailed evaluation that would require assessment of the relative importance of each attribute was not necessary.

3.3.7 Consideration of Other Factors (Step 7)

In addition to chemical and physical properties, several other factors are important in determining the final list of preferred candidate materials to be used in testing programs and preconceptual plug design schemes. These factors include economic availability, compatibility with various borehole diameters (ranging from several centimeters to as much as 10 m), and in the case of natural materials, proximity to the Hanford Site.

Each material ranked on the three lists derived from Step 6 for the three function classifications is evaluated in Step 7 with respect to these other factors. A final list of preferred candidate materials (Table I) is based on the physical and chemical properties evaluated in Step 6 and these other factors.

From the beginning of the selection process through Step 6, the evaluation procedure considered the physical and chemical properties of the materials on the original list and also considered the potential for determining these properties. Step 7 addresses limitations (such as cost or potential plug volume dependent on hole diameter) of the uses to which materials can be put. For example, certain materials that have desirable chemical and physical properties for performing certain plug functions may be costly (the precious metals are a good example). In other instances, materials that have desirable physical and chemical properties may only be appropriate for consideration as plugs in certain diameter holes (for example, the use of machined quartz or ceramic plugs for small diameter boreholes).

With the exception of Step 4, Step 7 is more qualitative and judgmental than the other steps in the evaluation. This subjectivity is necessary because questions of cost and availability are dependent on factors of plug environment and design that are not yet determined. In addition, the meaning of these terms is relative and depends on available alternatives at the time of actual plug placement. While it is almost certainly out of the question to use gold to plug a shaft or tunnel, it might be feasible to use it as part of a plugging system for a small borehole. Whether gold is, in

fact, too costly for this application depends partly on what alternatives to its use are available. If, for example, no other material had physical and chemical properties that were as suitable for a particular plugging function in a borehole, and if the plugging program required the function performance, then it is conceivable that a costly material would be used. In Step 7, the assessment that the cost will preclude the use of an expensive material is essentially an assessment that the hypothetical chain of events discussed above will not come to pass.

3.4 DISCUSSION

The final list of preferred candidate materials (Table I) derived from the approach described here is very similar to the list developed from the original selection process described in Taylor and others (1979). However, the approach presented in this chapter and in Appendix B is considerably different from the original process.

In general, the approach presented in this report helps clearly determine and organize those factors that are most significant to the final outcome of the selection process and documents the process in a more complete fashion. The reorganization of function classifications and more complete definition of attributes in this new approach makes it possible to compare materials that will have like applications in plug design and to discriminate between and rank them on common grounds.

The restructuring of the selection process also provides a framework for this type of analysis during future work on materials selection for repository backfill and canister hole plugs. New initial lists of materials for backfill and

canister hole plug problems could be developed, and the various attribute scales can be adjusted to reflect the more extreme physical and chemical conditions that may exist in the near-field environment of the waste storage canisters. It would probably be necessary to expand the list of material properties under the various function classifications if the selection scheme was modified to evaluate potential backfill and canister hole plug materials. For example, the thermal stability ranges of various materials may be a critical property in the near-field environment.

The list of preferred candidate materials developed by the selection process described by Taylor and others (1979) was verified by re-evaluation during the present study, as described here. This list is the basis for the physical and geochemical testing programs of preferred candidate materials presented in the next two chapters. This list is not intended to be a final list of potential candidate plug materials. In fact, additions and minor modifications were made as the two testing programs proceeded. However, materials on the list do represent the types of materials that are considered to have the greatest potential for successful use in plugs and for meeting the many other restrictions that may eventually be applied to plug design and to the entire borehole plugging problem.

4 GEOCHEMICAL TESTING PROGRAM

4.1 INTRODUCTION

4.1.1 Background and Objectives

Materials used in plugging boreholes must be stable in the plug environment over time periods that are long (many thousands of years) by any human standard of comparison. When engineered into plugs, these materials must block radionuclide migration to the biosphere as part of the overall containment function of the repository. One process that could lead to unacceptable levels of radionuclide migration to the biosphere during the containment period of the repository is chemical deterioration of plug materials due to reactions between the materials themselves or reactions with their surroundings.

The primary objectives of the geochemical testing program were to:

- Help define the behavior of candidate plug materials in the plug environment;
- Provide data on the relative stability and reactivity of candidate plug materials; and
- Identify the most promising materials for consideration in future studies involving plug system design and advanced testing programs.

Even though candidate plug materials from Table I are considered to be extremely stable and durable, slow chemical reactions not detected in earlier studies could eventually lead

to a loss in plug integrity. The need to make reliable predictions on behavior for periods of thousands of years or more places severe demands on any chemical testing program because long-term experiments may be necessary to obtain sufficiently accurate data on which to base these predictions.

However, given the large number of mixtures of candidate materials, which are of potential interest and could be designed from the list in Table I, and the need to reach early decisions on plug design, such long-term experiments are not practical at this stage of the program. Instead, the geochemical testing program described here is a series of initial screening tests that were intended to permit an evaluation of the suitability of materials based on their short-term chemical reactivities. These tests determined a lower bound on the level of reactivity to be expected over the useful life of the plug.

The results of these geochemical screening tests (described in this chapter) are combined with test results from the physical testing program (described in Chapter 5) to select a group of preferred plug materials (Chapter 6). This group of materials will be used in preconceptual design schemes to be described in a separate report. These materials should be subjected to more extensive chemical and physical testing in order to make the necessary long-term predictions on the behavior of materials in the plug environment.

4.1.2 Scope of the Geochemical Testing Program

Selection of tests for the present geochemical testing program was determined by estimates of environmental conditions to which the plug will ultimately be subjected. Preliminary ranges of temperature, pressure, pH, and ground-water

composition have been established (see Table A-I, Appendix A), and chemical degradation mechanisms for the plug materials were hypothesized and experiments were designed to detect the potential occurrence of reactions under these postulated environmental conditions.

Additional constraints on the selection of test procedures were: (1) the length of time available to do the tests; (2) the anticipated low reaction rates of plug materials; and (3) the availability of reaction vessels. The potential alteration mechanisms of plug material are: (1) chemical reactions between plug materials; (2) chemical reactions between the plug materials and the surrounding rock; (3) chemical reactions between the ground water and the plug materials (dissolution, selective leaching, solution-mediated phase changes or recrystallization); and (4) pressure-induced phase changes.

The rates of these reactions are likely to be extremely slow at plug seats, where temperatures are projected to range from the ambient wall rock temperature of 65°C to less than 100°C after closure of the repository (see Table A-I, Appendix A). Therefore, it was decided to run most tests at as high a temperature as was experimentally feasible to take advantage of the approximate doubling of reaction rates for every 23°C rise in temperature. A temperature of 250°C was selected for reasons discussed below. The assumption of a water-saturated repository required the tests to be done wet, which dictated the use of pressure vessels to contain the reactants. Equilibrium between the chromium in the stainless steel pressure vessel and oxygen in the test water maintained highly reducing conditions in the pressure vessels.

Thus, one of the major components of this program was a screening test for chemical reactivity of potential plug materials in contact with simulated ground water. Chemical alteration of the plug materials was detected by analysis of the solid and of the solution in contact with it after fixed periods at 250°C under saturated steam pressure.

Other experiments were designed to determine the effects of variables not tested in the procedure just described. For example, the solutions in all individual capsules were static, and a separate set of tests was run in a stirred pressure reactor on duplicate samples of some materials and mixtures to assess the effect of agitation on reaction rates. Likewise, the influence of hydrostatic pressure on reaction rates and phase transitions was evaluated for a selection of materials at 250°C and 34.5 MPa (5,000 psi). Some potential plug materials were tested under static saturated steam pressure at 150°C to examine the effects of temperature change on reaction rates. In general, the tests reflect extreme pressure, temperature, and moisture conditions at projected plug locations. In particular, temperatures at plug locations are not expected to exceed 100°C (see Appendix A, Table A-I), and any movement will be very slow and restricted. Thus, the laboratory tests reflect worst-case repository conditions with respect to several variables.

A further constraint was the need to evaluate approximately 40 samples for several reaction times. Physical limits on laboratory space and availability of pressure vessels necessitated that most materials be tested simultaneously in only a few vessels. This was accomplished by separately encapsulating the components of each individual test and placing all the capsules to be tested in the same vessel at a given temperature,

pressure, and length of time. Early in the process of designing the experiments, it was decided to encapsulate in PTFE (poly-tetrafluoroethylene) cells rather than to bear the cost of the more commonly used gold for a large number of tests. PTFE is chemically inert in contact with all anticipated reactants and is reportedly stable to 300°C. A test temperature of 250°C was chosen to provide the maximum acceleration of reaction rates consistent with the thermal stability of PTFE. The need to cool the entire autoclave to room temperature before sampling is an unavoidable consequence of any closed-tube experiment.

4.2 MATERIALS

4.2.1 Components

Materials used in both the geochemical and physical testing programs were selected from the list of preferred candidate plug materials developed during Task I work (Taylor and others, 1979). Chapter 3 describes a review and modification of the selection process that led to this list of preferred materials. The list of preferred plug materials presented in Table I resulted from this modified selection process and essentially confirms the original selection.

Appendix C of Taylor and others (1979) described a preliminary sample preparation scheme using preferred candidate plug materials (singly and in mixtures) that will serve specific functions in various parts of preconceptual plug systems. Materials from the preferred list (Taylor and others, 1979; Table I, this report) that are contemplated for use in solid, crystalline machined plugs (such as fitted crystalline quartz plugs or ceramic plugs) for small boreholes were not tested in

either the physical or the geochemical testing program. Materials tested in the initial programs (described in this chapter and Chapter 5) have potential use in multi-phase plugs designed from granular, natural materials and/or cements and concretes. The various samples constructed from these materials have potential application in all sizes of man-made accesses (small boreholes, shafts, and tunnels).

The sample descriptions presented by Taylor and others (1979) were derived with both the physical and geochemical testing programs in mind. The preliminary selection of samples described in that report (Taylor and others, 1979) is shown in Table III. The overall selection and design of samples in Table III were based on the projected or known engineering capabilities of materials from the preferred list of candidate materials.

Based on the list of preferred candidates (Taylor and others, 1979), 14 different materials were supplied by WCC for testing at SRI facilities. These final 14 materials were selected by preliminary screening tests performed at the WCC laboratory in Oakland, California, during the initial phases of the physical testing program; these tests are described in Chapter 5. Table IV presents the list of samples that were prepared from these materials and used by SRI in the geochemical testing program. Note the similarity between Tables III and IV; specific cements, cement additives, and the last category of eight unspecified samples (shown in Table III) were defined and acquired during the early part of this study.

Because it is difficult to detect the occurrence of chemical alterations without establishing an unreacted reference state, all 14 materials were thoroughly characterized using techniques

TABLE III^a

MATERIALS AND MATERIALS MIXTURES FOR PRELIMINARY
SAMPLE PREPARATION (DETERMINED BY TASK I WORK)

Basalt Samples

Bulk Basalt
Coarse-Grained Basalt
Fine-Grained Basalt
Basalt/Sand^b

Soil Materials

Oregon Bentonite^c
Wyoming Bentonite^c
Ringold Clay^c
Oregon Zeolite^d
Processed Bentonite

Soil Materials Mixtures

Oregon Bentonite/Sand
Wyoming Bentonite/Sand
Ringold Clay/Sand
Oregon Bentonite/Zeolite
Wyoming Bentonite/Zeolite

Basalt/Soil Materials Mixtures

Basalt/Oregon Bentonite
Basalt/Wyoming Bentonite
Basalt/Ringold Clay
Basalt/Sand/Oregon Bentonite
Basalt/Sand/Wyoming Bentonite
Basalt/Sand/Ringold Clay
Basalt/Zeolite/Oregon Bentonite
Basalt/Zeolite/Wyoming Bentonite
Basalt/Zeolite/Ringold Clay

Cement/Soil Materials/Basalt Mixtures

Portland Cement Type II/Sand/Basalt
Portland Cement Type V/Sand/Basalt
Portland Pozzolan Cement/Sand/Basalt
Hydrothermal Cement (1)/Sand/Basalt
Hydrothermal Cement (2)/Sand/Basalt
Portland Cement Type II/Zeolite/Basalt
Portland Cement Type V/Zeolite/Basalt
Portland Pozzolan Cement/Zeolite/Basalt
Hydrothermal Cement (1)/Zeolite/Basalt
Hydrothermal Cement (2)/Zeolite/Basalt

Eight Unspecified Combinations of Materials (From Table
B-XVI, Appendix B) in Water

^aFrom Taylor and others (1979)
^bGlaciofluvial sand from the Hanford Site
^cPrimarily smectite clay
^dPrimarily the mineral clinoptilolite

TABLE IV
SPECIMENS USED IN THE GEOCHEMICAL TESTING PROGRAM

<u>Sample ID No.</u>	<u>Composition</u>	<u>Proportions^a</u>	<u>Description^b</u>
1	Basalt		Single piece, polished face
2	Basalt		-10/+40 mesh
3	Basalt		
4	Basalt/sand	1:1	
5	Basalt/Oregon bentonite	1:1	Bentonite -325 mesh
6	Basalt/Wyoming bentonite	1:1	Bentonite -325 mesh
7	Basalt/Shurgel	1:1	Shurgel -325 mesh (processed bentonite)
8	Basalt/Aquagel	1:1	Aquagel -325 mesh (processed bentonite)
9	Basalt/Ringold clay ^c	1:1	Clay -325 mesh
10	Basalt/sand/Oregon bentonite	1:1:1	Bentonite -325 mesh
11	Basalt/sand/Wyoming bentonite	1:1:1	Bentonite -325 mesh
12	Basalt/sand/Ringold clay	1:1:1	Clay -325 mesh
13	Basalt/zeolite/Oregon bentonite	1:1:1	Zeolite, bentonite -325 mesh
14	Basalt/zeolite/Wyoming bentonite	1:1:1	Zeolite, bentonite -325 mesh
15	Basalt/zeolite/Ringold clay	1:1:1	Zeolite, clay -325 mesh
16	Oregon bentonite		-325 mesh
17	Wyoming bentonite		-325 mesh
18	Oregon bentonite/sand	1:1	Bentonite -325 mesh
19	Wyoming bentonite/sand	1:1	Bentonite -325 mesh

TABLE IV (continued)

<u>Sample ID No.</u>	<u>Composition</u>	<u>Proportions^a</u>	<u>Description^b</u>
20	Oregon bentonite/zeolite	1:1	Both -325 mesh
21	Wyoming bentonite/zeolite	1:1	Both -325 mesh
22	Oregon zeolite		-325 mesh
23	Ringold clay		-325 mesh
24	Ringold clay/sand	1:1	Clay -325 mesh
25	Fondu/sand/basalt	1:1:1	Fondu = hydrothermal cement (brand name)
26	Secar/sand/basalt	1:1:1	Secar = hydrothermal cement (brand name)
27	(Portland pozzolan cement + sand)/basalt	1:1	
28	(Portland Type II cement + sand)/basalt	1:1	
29	(Portland Type V cement + sand)/basalt	1:1	
30	(Fondu + zeolite)/basalt	1:1	
31	(Portland pozzolan cement + zeolite)/basalt	1:1	
32	(Portland Type II cement + zeolite)/basalt	1:1	
33	(Portland Type V cement + zeolite)/basalt	1:1	
34	(Portland Type V cement + silica flour)/basalt	1:1	
35	Basalt core + concrete		Bulk specimen supplied by Rockwell

TABLE IV (continued)

<u>Sample ID No.</u>	<u>Composition</u>	<u>Proportions^a</u>	<u>Description^b</u>
36	(TXI Chem Com cement + Lassenite)/sand	1:1	TXI Chem Com = portland cement with shrinkage compensating agent (brand name); Lassenite = natural pozzolan additive (brand name)
37	(Portland Type V cement + silica flour + Plastiment)/sand	1:1	Plastiment = organic water reducing retarder agent (brand name)
38	(Portland pozzolan cement + silica flour)/sand	1:1	
39	(Portland Type V cement + Lassenite)/sand	1:1	

^aAll proportions are by weight to ± 0.001 g.

^bAll materials ground to -200 +325 mesh, unless specified otherwise.

^cRingold clay from Unit D (see Chapter 5, Section 5.3.4.).

described in Section 4.4.2. The list of materials and the results of the analysis are given in Table V.

4.2.2 Design of Mixtures

Even though the same materials and mixtures of materials tested for physical properties in WCC's laboratory facility were tested at the SRI facility in Menlo Park, California, the specifics of sample preparation, sample size, and exact proportions of materials used in mixtures varied between the two laboratories in accordance with variations in testing equipment requirements and testing program objectives. The physical testing program examined a range of proportions of components in samples containing two or more of the materials listed in Table IV. This examination was done to help select the best proportions for optimum mechanical response of a given mixture. However, the geochemical program generally used simple mixtures with equal parts for two-, three-, and four-component systems. Chemical reactivities are generally not dependent on the percentage amount of a component present; one of the requirements of the chemical testing program at this stage was that only sufficient quantities of each component be present in order to prevent complete consumption of one of the components during the duration of the test runs.

Grain size also differed between samples used in the two testing programs. The physical testing program was designed to examine a range of grain sizes for most of the materials being tested. However, material for the geochemical testing program was finely ground (-200 to +325 mesh) in most, but not all samples, in order to maximize reaction rates between the small quantities being tested.

TABLE V
CHARACTERISTICS OF STARTING MATERIALS (GROUND TO -200 MESH)

Material	WCC No.	^a	^b range	Average Particle Size ^c	BET (m ² /g) ^d	Color	Mineral Phases ^e
Basalt	A-76	2.88	2.68 to 2.72	--		Dk.Gray	L,A,M
Bentonite							
Oregon	A-60	2.70	2.2 to 2.7	2.9	90	Brown	Mt
Oregon	A-61	2.67	2.2 to 2.7	2.9	90	Brown	Mt
Wyoming	A-04	2.44	2.2 to 2.7	7.3	25	Lt.Gray	Mt
Shurgel	A-03	2.47	2.2 to 2.7	5.9		Lt.Gray	
Aquagel	A-05	2.46	2.2 to 2.7	4.9		Lt.Gray	
Clay							
Ringold	A-77	2.71	2.6 to 2.7	2.6	45	Brown	
Rin-D							
Sand							
Glaciofluvial	A-79	2.64	--	-		Dk.Gray	L,A,Q
Quartz							
Silica Flour	A-84	2.68	2.65	3.1		White	Q
Zeolite							
Oregon	A-59	2.30	2.0 to 2.4	2.6	40	Lt. Brown	C
Oregon	A-73	2.20	2.0 to 2.4	2.6		Lt. Brown	
Portland Cements							
Type II	A-75	3.26	3.15	4.2		Gray	
Type V	A-01	3.16	3.15	5.7		Gray	
Pozzolan	A-02	3.15	--	3.2		Gray	
Hydrothermal Cements							
Fondu	A-74	3.34	--	4.1		Dk.Brown	
Secar	A-83	3.06	--	3.3		White	

^a Measured experimentally with the pycnometer (g/cm³)
^b From literature (g/cm³)
^c Fisher Subsieve Analysis (microns)
^d Surface area measurement (see Section 4.4.2.1)
^e Found by powder x-ray diffraction analysis (using standards)
L = Labradorite (Ca,Na)Si₂Al₂O₈; A = Augite (Ca,Mg,Fe)•SiO₂; M = Ti-Fe Magnetite (Fe,Ti)Fe₂O₄;
Mt = Montmorillonite; Q = Quartz SiO₂; C = Clinoptilolite (Ca,Na,K)Al₂Si₇O₈•6H₂O

Thus, mixtures for geochemical testing were prepared by combining materials in equal proportions by weight. For example, the basalt/sand mixture was half sand and half basalt, and the basalt/sand/zeolite mixture was one-third basalt, one-third sand, and one-third zeolite. Materials, such as basalt and sand, that were received by SRI in a relatively coarse state were ground, and the -200 to +325 mesh fraction was used for making the mixtures. Other components, such as clay, bentonite, and zeolite, occur naturally as fine particles. These were ground to break up agglomerates, and the -325 mesh fraction was then used in the mixtures being tested. Specimens containing cement were prepared by separately casting and curing the specified cement/aggregate compositions. They were then ground to -200 to +325 mesh and combined with equal proportions of the other ingredients. Some of the cements were supplied as pre-cast cubes by the WCC laboratory in Oakland, California. Several one- and two-component specimens were tested, even though they are not candidates for plug systems; such testing was done to understand better the potential alterations and reactions in more complex mixtures and to help simplify the analysis of complex mixtures. The list of starting materials used in mixtures for geochemical testing is given in Table V. This table also gives some of the characteristics of these individual starting materials.

4.3 TYPES OF TESTS

4.3.1 250°C Static Test

The geochemical test involving the largest number of samples was a 250°C, static experiment conducted in a 11.4-liter stainless steel autoclave. Three identical sets of the 39

samples listed in Table IV were tested in the autoclave, with a complete group being removed after one-, two-, or three-month exposures to the hydrothermal conditions. Temperature control was achieved by external strip heaters powered by a Honeywell-Brown controller. The test temperature in the interior of the autoclave was monitored continuously by two thermocouples connected to a two-pen strip-chart recorder. One thermocouple was adjusted so that its junction was at top center on the central axis of the vessel; the other was placed about 2.5 cm from the bottom, near the vessel wall. Temperature control was maintained at $250^{\circ} \pm 3^{\circ}\text{C}$ during the three-month duration of the test. The two thermocouples agreed within 4°C , indicating the temperature gradient in the autoclave was very small. During operation, the pressure inside the autoclave was equal to the pressure of water in equilibrium with its vapor at that temperature, or about 3.9 MPa at 250°C , as indicated by a pressure gage connected to the vessel.

The specimen bottles were arranged in tiers on stainless steel racks in the autoclave so that when it was cooled at the end of each one-, two-, or three-month test period, all the bottles from a given group could be easily removed without disturbing the others. Synthetic ground water was prepared (as described in Section 4.4.1.3) and added to the autoclave in the space surrounding the specimen bottles. Sufficient head space was left in the vessel to allow for thermal expansion of the water. The autoclave was brought to temperature at a rate of about 60°C per hour at the beginning of each run, whereas the natural cooling rate (when the runs were terminated) was approximately 15°C per hour due to the large thermal mass of the autoclave.

4.3.2 150°C Static Test

The 150°C tests were conducted in a 2-liter Parr Instruments Corporation general purpose autoclave with associated heater, temperature controller, and pressure gage. The autoclave is constructed of Hastelloy C, which gives it a somewhat higher pressure capability than the standard 304 stainless steel alloy. The temperature of the autoclave was monitored near its central axis about a third of the way up from the bottom, using the unit's built-in thermocouple well. The temperature was held constant to within $\pm 2^\circ\text{C}$ over the duration of the test. The pressure was equal to the steam-saturated vapor pressure of water at 150°C, or about 0.5 MPa. The autoclave was filled with the simulated ground water used in other tests. Because of the smaller size of this autoclave, only 18 specimen bottles could be accommodated for the test run. Accordingly, samples 12, 13, 21, 25, 27, and 29 (mixtures of basalt and other natural materials and various cements plus basalt as an aggregate) were selected from the list in Table IV and prepared in three identical sets. One set was removed from the autoclave after each of the one-, two-, and three-month test periods.

4.3.3 Static High Pressure 34.5 MPa Tests

A Parr Instruments Corporation 1-liter high pressure autoclave was used to determine the effects of high pressure on the reactivities of plug materials in a hydrothermal environment. Except for its smaller capacity and higher pressure capability, the autoclave is similar to the one used for the 150°C static tests in that they both are constructed of Hastelloy C and have similar heaters, controllers, thermocouple placement, and pressure gages.

Only one specimen at a time could be tested in the high-pressure autoclave. By contrast, it was possible to run multiple samples simultaneously in the 150°C and 250°C tests just described, because under the conditions of those experiments, there was no pressure difference between the interiors and the exteriors of the PTFE bottles in which the samples and solutions were sealed. In a high-pressure experiment, a sealed PTFE bottle containing water would have an internal pressure equal to the steam-saturated vapor pressure at the reaction temperature, whereas the external pressure would be that set for the experiment, which in this case was 34.5 MPa. If gold cells had been used, they would have deformed under the external pressure without failing; however, as discussed earlier, gold cells were not used in this research for reasons of cost. Such a pressure difference would crush a PTFE sample bottle, causing it to leak and to mix with the water in the autoclave. (The more commonly used gold cells do not have this problem because the ductile metal can deform under an external pressure without failing.) Without encapsulation to isolate the samples, it is not possible to test more than one sample at a time. Therefore, for the high pressure tests, single specimens chosen from the list in Table IV were placed in the autoclave with the standard test solution (Section 4.4.1.3). The ratio of 40-g solid per 400-ml test solution was used to keep the solid-to-liquid ratio identical for all the tests.

After the autoclave was sealed, it was heated to 250°C without applying any external pressure. Once the temperature stabilized, the vessel was pressurized with argon to 34.5 ± 0.34 MPa using an external intensifier system. Invariably, a minor drop in pressure of about 1.4 MPa occurred over the first 12 hours

of operation, at which time the system was repressurized to 34.5 MPa. No further pressure drops were observed during the remainder of the two-week test period.

4.3.4 250°C Stirred Tests

The effect of continuous sample agitation on sample reactivities was tested using a Pressure Products Industries 1-liter, 304 stainless steel, magnetically coupled, stirred autoclave. The design of the autoclave precluded testing several samples simultaneously. Hence, 40 g of a given solid was placed in the autoclave with 400 ml of test solution (simulated ground water) and run at $250^{\circ} \pm 3^{\circ}\text{C}$ and 3.9 ± 0.2 MPa for two weeks with continuous stirring at about 500 rpm. The temperature was monitored using a strip chart recorder connected to a thermocouple inserted in the vessel's integral well. Heating was provided by a mantle that fastened around the autoclave; the temperature was controlled with a Norton unit.

4.4 TESTING PROCEDURES

A brief description of sample preparation, testing, and analytical procedures is included here. Further details are available in project files at the SRI facilities in Menlo Park. The various procedures applied by SRI generally reflect the standard laboratory practice. Equipment operation and calibration is based on descriptions provided by the manufacturer and experience of the technical personnel performing the analyses. Special procedures, such as sample preparation and encapsulation, are discussed here and were also included in the project file of procedures in SRI.

4.4.1 Sample Preparation

4.4.1.1 Grinding

Some of the materials provided to SRI, such as the Oregon bentonite, zeolite, and silica flour, were -325 mesh. Others, such as the basalt, glaciofluvial sand, Ringold clay, and Wyoming bentonite, required grinding to reduce the particle size or to break up agglomerates. Those substances were ground by hand in an alumina mortar and pestle and then screened to collect the -200 to +325 mesh fraction. The sized powders were dried in a 60°C oven where they were stored until needed.

4.4.1.2 Polishing

The bulk basalt specimens (Sample No. 1, Table IV) were made by slicing with a diamond saw to form cubes approximately 1 cm on a side. One face of each specimen was polished by standard metallographic procedures using a series of progressively finer abrasive grits, finishing with 0.3 micron diamond paste. Optical and scanning electron micrographs (Section 4.4.2.5) were taken of the polished surfaces.

4.4.1.3 Test Water Preparation

The test water was synthesized as a single 50-liter batch according to a recipe supplied to WCC by Rockwell. This recipe is based on Ames (1978). Appropriate amounts of the following salts were dissolved in deionized water in a polyethylene carboy to give the indicated concentrations: hydrated calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), 23.0 mg/l; hydrated magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), 8.3 mg/l; sodium bicarbonate (NaHCO_3), 109.6 mg/l; and potassium sulfate (K_2SO_4), 20 mg/l. The pH of

the resulting simulated groundwater was found to be 8.12. Cations were analyzed by atomic absorption spectroscopy when the solution was first prepared and at 1-month intervals afterward. The cationic concentrations at 1-month intervals proved to be the same as those measured in the initial analysis of the simulated ground water.

4.4.1.4 Encapsulation

During the initial stages of the program, several Rockwell scientists expressed concern that, if the solids were freely in contact with test solutions, it would be impossible to distinguish between species that precipitated out of a supersaturated solution on cooling and those that formed at a higher temperature due to reaction with the solution. Accordingly, solids were encapsulated in a semipermeable membrane that would allow dissolved species to exchange with the test solution while retaining any solids. A commercially available filter membrane that met the necessary requirements was used in lieu of perforated gold foil.

The solid specimens were bagged in pieces of a porous, PTFE filter membrane (Zitex, Chemplast, Inc., Wayne, New Jersey) tied with 0.25-mm platinum wire. For all specimens, 1.50-g total weight of solids was used. The Zitex membranes are chemically inert toward any of the substances used in this test program and are made with a variety of pore sizes. The ones used here had pores in the 10 to 20 micron range. Zitex is hydrophobic; water will not pass through it at room temperature in the absence of a pressure differential. In the hydrothermal experiments, however, the contents of the Zitex bags were always wet when they were analyzed at the conclusion of each experiment, indicating that water did pass through.

The Zitex bags were placed with 15 ml of the test solution in 30-ml (nominal), screw-top bottles made of perfluoroalkoxy (PFA)-substituted PTFE (Cole-Parmer Instrument Company, Chicago, Illinois). That quantity of solution gave sufficient head space to accommodate the thermal expansion of water between room temperature and 250°C. PFA-substituted PTFE, unlike conventional Teflon, is thermoplastic and can be deformed and molded with sufficient application of heat. Special tubular resistance heaters were constructed with an inner diameter a few millimeters larger than the outer diameter of the bottle caps. These heaters were set at 350° to 375°C, at which temperature the PFA-substituted polymer is fairly fluid. Before the lids could be heat-sealed to the bottles, however, the surface contacts had to be treated with a proprietary etching agent used in the plastics industry (Tetraetch, R.S. Hughes Company, Sunnyvale, California) to enhance the bonding of the two surfaces. To minimize evaporation of the test solution, the bottle and its contents were frozen in dry ice before the lids were sealed. The frozen bottles were inserted so that just their lids were in the hot zone of the heater. Within about 5 minutes, the lid and top of the bottle were hot enough to form a seal when pressure was applied by screwing down the lid further and then pressing a steel plate on top. Many trials were required to establish the technique, but eventually SRI technicians were able to reliably seal the bottles.

4.4.1.5 Preparation of Hydraulic Cement Mortars

ASTM method C-109 (American Society of Testing and Materials [ASTM], 1977a) was followed to prepare the cubic cement specimens. Because of the small quantity (5 to 10 g) of material

needed (one cube of each was more than sufficient), the European standard hand-mixing procedure was used in place of the ASTM mechanical mixing method, which is more appropriate for mixing larger volumes of cement. The weight ratios used in mixing were:

- Cement/sand/water = 1:2.75:0.5;
- Cement/zeolite/water = 1:2.5:1.39.

The cement and sand were premixed and spread on a flat surface, and the water was placed in a shallow depression formed in the powder surface. The wet mortar was vigorously mixed with a spatula following the ASTM C-109 procedure (ASTM, 1977a). The samples were allowed to set in air under wet towels for 4 hours. They were then submerged in a water bath at 95°C for a period of 36 to 42 hours to accelerate their aging. The cubes were crushed in a Baldwin press and reduced to -7 mesh with a steel mortar and pestle. Final portions, weighing 25 g each, were then ground to -200 mesh.

4.4.2 Pre-Test Examination and Sample Characterization

4.4.2.1 X-Ray Powder Diffraction Analysis

A thin layer of each specimen, ground to -200 mesh or finer, was spread on a piece of two-sided Mylar tape, which was supported by a glass slide. X-ray diffraction patterns were generated on a Phillips x-ray diffraction unit employing a high intensity copper tube, a compensating theta slit, a vertical goniometer, and a pyrolytic graphite monochromator. The x-ray data were processed through a Canberra solid state manipulation and data reduction system. Each sample was scanned from 3 to 90 degrees two theta at 10 degrees per minute. Stereoscans of

significant two-theta areas were recorded at 1 degree per minute. Patterns could be obtained for crystalline species present in amounts of at least 1 percent by volume, which is the detection limit of the particular apparatus used in these tests. A major limitation on analyzing x-ray data from mixtures containing many components is that frequently, a significant number of diffraction lines are superimposed and cannot be resolved.

4.4.2.2 Brunauer, Emmett, and Teller Analysis

Surface area measurements were made by the dynamic Brunauer, Emmett, and Teller (BET) method (Brunauer and others, 1938) in which nitrogen (N_2) gas, diluted about 10 to 1 in a helium (He) carrier, adsorbs on the surface of the solid at low temperatures. Monolayer coverage is assumed, and the surface area can be estimated by measuring the quantity of N_2 desorbed on heating from -196° to $127^\circ C$. Comparison standards of carbon (surface area approximately equal to $100 \text{ m}^2/\text{g}$) and titanium oxide (TiO_2 ; surface area approximately equal to $10 \text{ m}^2/\text{g}$) were run to calibrate the instrument. The smallest surface area that can be measured using this technique is $1 \text{ m}^2/\text{g}$.

4.4.2.3 Fisher Subsieve Analysis

Average particle sizes of the powders were also measured on a Fisher Subsieve Sizer, which operates on the principle that a plug of coarse powder is more permeable to diffusion of a gas than is a plug of fine powder. This measurement requires that the densities of the solid particles be known; such densities were obtained using a Micrometrics (Model 1303) helium-air pycnometer. Average particle sizes in the range 0.2 to 50 microns can be determined by this method.

4.4.2.4 Petrographic Analysis

Thin sections of bulk basalt were cut and polished in the petrographic laboratory at Stanford University, Stanford, California. These sections were then analyzed at SRI using a Leitz petrographic microscope.

4.4.2.5 Scanning Electron Microscopy

A Cambridge Stereoscan scanning electron microscope (SEM) was used to examine some of the solids tested in this program. One of the main advantages of the SEM is its ability to produce high magnification images with good depth of field. This allows study of microstructural features, such as grain sizes, porosity, etc. Color rendition is impossible because the image is produced by electrons rather than photons. Polished faces or, occasionally, acid-etched polished faces of bulk specimens (such as basalt) were examined using this method. Powdered materials were analyzed without further preparation. A Kevex energy-dispersive x-ray analyzer accessory on the SEM permitted semiquantitative analyses for elements of atomic number 12 or greater.

4.4.3 Post-Test Examination and Sample Characterization

Because one of the objectives of this test program was to evaluate changes occurring as a result of hydrothermal exposure, solid materials recovered after the tests were subjected to the same analyses that were described in Section 4.4.2.

4.4.3.1 Solution Analysis by Atomic Absorption (AA) Spectroscopy

Specimen bottles removed from the autoclaves were opened by drilling a small hole through each cap. A hypodermic syringe was inserted through the hole, and a 3-ml aliquot portion of solution was removed and injected into a polyethylene bottle containing 57 ml of deionized water acidified with two drops of nitric acid (HNO_3). The remainder of the liquid was removed volumetrically and transferred to another container for storage. The bottle caps were cut off with a hot wire loop and the solid contents were placed in a 60°C oven for drying prior to further analysis.

The collected sample solutions were analyzed for sodium, potassium, magnesium, calcium, iron, aluminum, and silicon (Na, K, Mg, Ca, Fe, Al, and Si) according to ASTM Method D 2576-76 (ASTM, 1978b). This method depends on the fact that metallic elements in their ground states absorb light of the same wavelength as they emit when excited. When radiation from a given excited element passes through a flame containing ground state atoms of that element, the intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the flame. Because the wavelength of the light beam is unique to the metal being determined, the radiant energy absorbed by the flame is a measure of the concentration of that metal in the sample. Radiation was provided by a lamp with a hollow cathode constructed from the element to be determined. The sample is aspirated into an oxidant-fuel flame through which the beam passes. A monochromator isolates the characteristic radiation from the hollow cathode lamp, and a photo-sensitive device measures the attenuated transmitted radiation.

Calibration curves were constructed according to ASTM Method D 2576-76 (ASTM, 1978b) for each of the elements to be analyzed by preparing a series of standard solutions, each with a known concentration of the particular species. The concentrations were chosen to span the range expected for the unknowns. The absorbance of each solution was then measured, and a curve was constructed relating the experimentally determined value to the concentration of the solution. The calibration curves were linear. In a similar way, the absorbance of each test solution was measured, and only a single measurement was made for a particular element in a given sample. The concentrations of each of the sought-for elements were then calculated using the calibration curves.

A Varian-Techtron AAG atomic absorption spectrophotometer was used to analyze for Na, K, Mg, Ca, and Fe. An accessory graphite furnace CRA-90 atomizer was used for the Al and Si analysis because those elements were present in concentrations too low for detection with the standard flame burner. From past experience with many similar analyses, SRI technicians know that the precision of the AA spectrophotometer operating in the conventional flame mode is about 1 percent (2 sigma), whereas with the graphite furnace it is about 20 percent (2 sigma). The operating conditions used during experiments are shown in Table VI.

4.5 RESULTS

Results and detailed data from the geochemical testing program are tabulated in Appendix C, Tables C-I to C-XIII.

TABLE VI

OPERATING CONDITIONS FOR ATOMIC ABSORPTION ANALYSIS

<u>Metal</u>	<u>Wavelength (10^{-9}m)</u>	<u>Fuel (Acetylene)/ Oxidant</u>	<u>Standard Concentration Range (ppm)^a</u>	<u>Detection Limit^b</u>
Sodium	589.0	C ₂ H ₂ /air	0.1 to 0.5	0.025 ppm ^a
Potassium	766.5	C ₂ H ₂ /air	0.25 to 2.00	0.01 ppm
Magnesium	285.2	C ₂ H ₂ /air	0.05 to 0.4	0.01 ppm
Iron	248.3	C ₂ H ₂ /air	0.5 to 10	0.2 ppm
Calcium	422.7	C ₂ H ₂ /air	0.25 to 2.0	0.05 ppm
Aluminum ^c	309.3	C ₂ H ₂ /air	5 to 40	2 ppm (flame) 0.02 x 10 ⁻⁹ g (graphite)
Silicon ^c	251.6	C ₂ H ₂ /N ₂ O	0.5 to 20	5 ppm (flame) 0.02 x 10 ⁻⁹ g (graphite)

^aParts per million (mg/l).

^bThe detection limit is usually considered to be equal to twice the maximum variation of the background.

^cGraphite furnace temperature program:

dry temperature: 125°C; 50 seconds.

ash temperature: 500°C; 20 seconds.

atomize temperature: 2,600°C; hold time 1.5 seconds, ramp rate 600°C/sec.

4.5.1 General Observations

When the 11.4-liter autoclave was opened after the 1-month test at 250°C, some of the PTFE bottles used to encapsulate the samples had failed. Each of those bottles was characterized by one or two longitudinal cracks and a quantity of test solution different from the 15 ml it originally contained. Although the mechanism of bottle failure has not been proved, a plausible explanation has been developed. When the temperature in the autoclave first was raised to 250°C, the solutions in each of the bottles expanded to fill the head space that had been left, compressing in the process the air that had originally been sealed in the bottles. It is well known that at high temperatures, PTFE is permeable to diffusion of molecular gases, and it is likely that at 250°C the compressed air diffused out of the bottles during the test runs. Later, when the autoclave cooled, a partial vacuum was created in the bottles as the solutions underwent thermal contraction. Back-diffusion of air was not rapid enough to fill the evacuated space. Moreover, because PTFE, like all thermoplastics, softens at elevated temperature, the bottle walls would have collapsed inward. This hourglass shape due to wall collapse was observed in many of the bottles after testing. The cracks resulted from deformation that exceeded the failure strength of the material.

Whether the surrounding test solution entered or was expelled from a particular bottle depended on the temperature at which the crack occurred and the position of the bottle in the autoclave vessel. Because the necessary head space in the 11.4-liter autoclave was conservatively overestimated, the top tier of sample bottles was exposed only to saturated steam during the first month's test. Cracks in those bottles would

have allowed solution to leak out. Those further down in the vessel were submerged in test solution, and they could have gained liquid after cracking as subsequent thermal contraction of the fluid created a partial vacuum in the bottles.

Apparently the likelihood of failure was also influenced by manufacturing variations in the sample bottles. Bottles were used from at least four separate shipments from the manufacturer, and some of them evidently were not as strong as others. Those obtained in the first two shipments were prone to failure, whereas none of the bottles from the last shipment failed, even though all batches experienced about the same degree of deformation after cooling. The bottles were not analyzed to verify this possible variation in properties. About one-third of the bottles tested at 250°C in the 11.4-liter autoclave showed evidence of cracking. At lower temperatures there was no problem with PTFE encapsulation, as indicated by the absence of cracking in bottles used in the 150°C tests.

All the specimen bottles were examined each time the autoclave was opened. All those destined for further testing and showing signs of failure were opened, and the contents were re-encapsulated in new PTFE bottles. Where less than the original 15 ml of test solution was present, the new bottles were topped up to 15 ml, and the quantity of added test solution was recorded. Where a greater quantity of test solution was present, the excess was removed, the amount was recorded, and in some cases, it was submitted for AA analysis along with the other samples. The results of those analyses are given in Table C-V of Appendix C.

4.5.2 Single Natural Materials

The most comprehensive data on these materials (basalt, bentonite, zeolite, and Ringold clay: sample nos. 1, 2, 3, 16, 17, 22, and 23 from Table IV) were obtained from the 250°C static test in the 11.4-liter autoclave. The results of AA analysis of the solutions are given in Tables C-II, C-III, and C-IV of Appendix C. The results of qualitative x-ray phase analysis of the solids remaining after testing are given in Table C-VIII, and the quantities of solids recovered from the Zitex filter bags after drying are listed in Table C-XI. As shown by AA data, the leaching behavior of all these materials is similar. Ionic concentrations in the solutions fall generally in the ranges: Na equal to 50 to 150 ppm (parts per million); K equal to 2 to 20 ppm; Mg less than or equal to 2 ppm; total Fe less than or equal to 10 ppm; Ca equal to 2 to 40 ppm; Al less than or equal to 5 ppm; and Si equal to 50 to 200 ppm. There are some anomalous data, most of which are explained by solution loss from cracked bottles. Except for Al, there seems to be little effect from increased time at temperature. Overall, the concentrations are low and show that the solids are fairly stable under the given test conditions.

In any closed-tube experiment, such as those discussed here, there is the possibility that species will precipitate out of solution when the autoclave is cooled so that subsequent solution analysis inaccurately portrays conditions at temperature and pressure. Recent experiments at Stanford University, conducted by Mr. Raynald Gillemette, show that for the basalt-water system any quench taking longer than 20 to 30 minutes will cause precipitation. It was in partial recognition of this phenomenon that individuals from Rockwell recommended wrapping the solids in porous

membranes. It was stated that phases precipitating during the quench could be readily identified by their distinctive morphologies and from the fact that they would be found predominantly outside the membrane. Quench phases of that sort were not observed in any of the experiments discussed here.

The behavior of silica in hydrothermal systems has been studied extensively and it is instructive to consider it at this point, since all the materials tested contained SiO_2 in one form or another. The maximum Si concentration in solution at equilibrium is given by the known solubility of amorphous silica. Data from the literature (Fournier and Truesdale, 1973) are: 250°C: $[\text{SiO}_2]=1,200$ mg/l; 50°C: $[\text{SiO}_2]=200$ mg/l; 25°C: $[\text{SiO}_2]=100$ mg/l. In terms of elemental concentrations, as used in this report, the concentrations are: 250°C: $[\text{Si}]=561$ mg/l; 50°C: $[\text{Si}]=93$ mg/l; 25°C: $[\text{Si}]=47$ mg/l. It can be seen by reference to the tables in Appendix C that in almost all cases the silicon concentrations fall between those given by amorphous silica solubility at 250°C and 25°C. The most notable exceptions are the Si concentrations of 540 and 580 mg/l found for two of the stirred tests (Appendix C, Table C-VII). Given that the cooling rate of the stirred autoclave was almost as slow as that of the 11.4-liter autoclave, these concentrations, which are near the 250°C amorphous SiO_2 solubility, indicate that the lower values from the static tests are due to low reactivities rather than precipitation during the cool-down period. This also is consistent with results from Stanford University reported by Mr. Raynald Gillemette.

One consistent finding is the presence of high-calcium concentrations in solutions containing Oregon bentonite. Agitation greatly accelerates the leach rates, as can be seen

from the data in Table C-VII of Appendix C. By contrast, the 34.5 MPa, 250°C static test produced only a modest enhancement in leaching rates. There is no significant temperature effect on leaching rates, as indicated by the overlap of solution concentrations for the 250°C and 150°C tests (Tables C-II, C-III, C-IV and C-VI; Appendix C).

The results of x-ray diffraction analyses indicated that the solid phases remaining in the PTFE membrane bags are only slightly changed as a result of hydrothermal exposure at 250°C. Reference to Figure 2 and to Table C-VIII of Appendix C shows that a small amount of montmorillonite formed in the basalt over time, probably from the glassy fraction, because the ratios of the other crystalline phases remained the same. SEM examination of the surfaces of basalt cubes also showed the presence of montmorillonite (Figure 3). The tabular crystals in the photo micrograph are an aluminum silicate present in concentrations too low for x-ray diffraction analysis. Figure 3(a) also shows that the basalt surface has been etched by the test solution to a slightly roughened state from its originally polished condition. All the basalt phases were attacked to about the same extent, although labradorite may have been slightly more resistant.

The two-week, stirred test at 250°C showed that there is a strong tendency for powdered basalt to cement and form a rigid mass. About half the sample recovered from the autoclave after testing was in a single, strong, dense piece (Figure 4). The remainder was still in its original, finely-divided state. X-ray diffraction analysis (Figure 5) shows that cemented material has a broad diffuse halo centered around 25 degrees two theta. This indicates that amorphous or microcrystalline quartz has formed, probably by reprecipitation of material

(a) STARTING MATERIAL

(b) SAMPLE 3C, 1 MONTH

NOTES: A = Augite; L = Labradorite; M = Magnetite; Mt = Montmorillonite

FIGURE 2
X-RAY DIFFRACTION SPECTRA OF
BASALT TESTED UNDER 250°C,
STATIC CONDITIONS

(c) SAMPLE 3B, 2 MONTHS

(d) SAMPLE 3A, 3 MONTHS

NOTES: A = Augite; L = Labradorite; M = Magnetite; Mt = Montmorillonite

FIGURE 2 (CONTINUED)

FIGURE 3

PHOTOMICROGRAPHS OF THE SURFACE
OF A BASALT CUBE BEFORE AND AFTER
3 MONTHS IN 250°C STATIC SOLUTION

(a) CEMENTED BASALT

(b) CEMENTED BASALT AND BENTONITE

FIGURE 4
PHOTOGRAPHS OF MATERIALS FROM
AUTOCLAVE STIRRED TESTS

(a) CEMENTED BASALT

(b) UNCONSOLIDATED MATERIAL

NOTES: A = Augite; L = Labradorite; M = Magnetite; Q = Quartz

FIGURE 5

X-RAY DIFFRACTION SPECTRA OF
BASALT FROM STIRRED 250°C TESTS

dissolved from the glassy fraction. SEM analysis shows intergranular regions containing silica (SiO_2), which may be responsible for the cementing action. The unconsolidated residue gives an x-ray spectrum similar to that of powdered basalt (Sample 3) after one-month exposure (Table C-VIII of Appendix C). The x-ray spectrum of material from the high pressure test (Figure 6) is very similar to the spectrum of material from the stirred test (Figure 5).

Other x-ray analyses show that the quartz in the Oregon bentonite decreases in concentration as a small quantity of montmorillonite forms. The x-ray spectra for the Wyoming bentonite and the Ringold clay tested for three months at 250°C under static conditions contain, in addition to the expected patterns, a single unidentified large peak with a d-spacing of 3.18 angstroms. Apparently a species has formed with a high degree of preferred orientation that accentuates a single peak in its x-ray spectrum. The 100-percent peak in the x-ray spectrum of labradorite falls at 3.18 angstroms; however, there is no obvious structural reason it should form with such a high degree of preferred orientation. Without the presence of other peaks, identification by x-ray diffraction cannot be made. As with the solution analyses, the x-ray data show only a modest reactivity for these materials under the test conditions.

4.5.3. Mixtures of Natural Materials

Most of the data on mixtures of natural materials (basalt plus sand, clay and/or zeolite, and mixtures of clay with sand or zeolite: Sample Nos. 4 to 15, 18 to 21, and 24 from Table V) were obtained from the 250°C static, hydrothermal test. Results were very similar to those discussed in the preceding section. Atomic absorption (AA) analysis of solutions

NOTES: A - Augite; L - Labradorite; M = Magnetite; Mt = Montmorillonite

FIGURE 6
X-RAY DIFFRACTION SPECTRUM OF
BASALT FROM STATIC, 34.5 MPa,
250°C, 2-WEEK TEST

recovered from the test bottles generally fell into the same ranges found for the single components, with Na equal to 50 to 150 ppm; K equal to 2 to 20 ppm; Mg less than or equal to 2 ppm; total Fe less than or equal to 10 ppm; Ca equal to 2 to 40 ppm; Al less than or equal to 5 ppm; and Si equal to 50 to 200 ppm. Mixtures containing Oregon bentonite showed the highest leaching rates and were above the levels just quoted. Under the conditions of these tests, there is little or no effect on leaching behavior due to time at temperature (Tables C-II, C-III, and C-IV, Appendix C), change in temperature (Tables C-II, C-III, C-IV, and C-VI) or increased pressure (Table C-VII). There is a significant acceleration of leaching rates as a result of agitation (Table C-VII). For example, powdered basalt shows more than a ten-fold increase in leaching rates in the stirred experiments, based on a comparison of the silicon concentrations in solution for a sample of powdered basalt run under static conditions at 250°C for one month (Appendix C, Table C-II) and for stirred basalt.

X-ray diffraction analysis of these mixtures is more complicated than for the single component specimens. The general conclusion is that any little change occurs in the solid mixtures as a result of hydrothermal exposure. Because the spectrum for each mixture is a superposition of the spectra for each of its components, many peaks are present, and there is considerable overlap among them. As a result, evidence for low concentrations of alteration products is often obscured, and the detection limit for the appearance of new phases is close to 3 to 5 volume percent rather than the one volume percent for pure materials. The one consistent observation is that small amounts of montmorillonite formed in mixtures containing basalt under the 250°C static test conditions (Table C-IX, Appendix C). With a few exceptions, Fisher

subsieve particle size analyses show a modest decrease in particle size in the powders over the 3-month test at 250°C and a slight decrease in porosity as the bagged powder compacts. The latter result probably is due to particle re-arrangement, which produces higher packing densities.

4.5.4. Mixtures Containing Cements

Atomic absorption (AA) analysis of solutions from 250°C static tests of these materials (various cements with sand or zeolite and basalt as aggregate, and cements with these ingredients plus additives: Sample Nos. 25 to 39 from Table IV) gave results that differed very little from those obtained from the other specimens in this program. Test solutions from mixtures containing cements generally had the lowest Na concentrations of all those tested. Ionic concentrations for some specimens after a 1-month exposure to hydrothermal conditions were higher than tests that ran for two and three months, possibly due to incomplete curing before the start of the autoclave experiments. This is borne out by the x-ray results (Table C-X, Appendix C) which show differences in the spectra between the untested and the 1-month specimens, with little or no change thereafter. Due to the multiplicity of phases and extensive overlap of peaks, the x-ray spectra are difficult to interpret in greater detail. The particle sizes and porosities follow the same trends as for all the other materials tested, (i.e., both decrease slightly with time at temperature).

4.6 DISCUSSION AND SUMMARY

4.6.1 General Considerations

All of the materials examined during testing were relatively stable under test conditions. Analysis of solutions resulting

from exposure to hydrothermal conditions gave the following ranges of ionic concentrations for most materials: Na, 50 to 150 ppm; K, 2 to 20 ppm; Mg, less than or equal to 2 ppm; Fe, less than or equal to 10 ppm; Ca, 2 to 40 ppm; Al, less than or equal to 5 ppm; and Si, 50 to 200 ppm. For some specimens, higher Na and K solution concentrations may have resulted from soluble alkali compounds present as contaminants. Dissolved silicon and aluminum, on the other hand, could have originated only from breakdown of the aluminosilicate networks present in most rock-forming minerals. Solution concentrations of Si and Al are therefore considered to be of more significance as indicators of mineral reactivity than are concentrations of other ionic species.

Results from glass leaching experiments can put into perspective the degree of hydrothermal reactivity found in these geochemical tests. A soda-lime-silica glass composition (similar to window glass) exposed to a static volume of distilled water for seven days at 100°C gave a dissolved silica concentration of 600 ppm (Clark and others, 1976). Fused silica similarly exposed for 10 days at 25°C gave a dissolved silica concentration of 60 ppm (Wirth and Gieskes, 1979). Both glass tests were conducted under considerably less severe conditions than the hydrothermal experiments performed here. However, Si concentrations up to an order of magnitude greater were reported for the experiments on glass. X-ray diffraction analysis of the solids performed after test runs during this geochemical testing program also showed that little reaction had occurred in the samples.

4.6.2 Discussion of Single Natural Materials

Basalt solution concentrations were in the ranges quoted above for the 250°C and 150°C static hydrothermal tests. Agitation

in the 2-week stirred tests produced significantly higher ionic concentrations in solution. X-ray analysis of the solid residue from the static tests showed a limited formation of montmorillonite, and SEM examination showed that the montmorillonite was present as a platy surface layer on the basalt particles.

Agitation of basalt under hydrothermal conditions caused the powdered basalt particles to aggregate and eventually to cement together. The x-ray spectra from the cemented basalt contained a broad halo characteristic of an amorphous or microcrystalline structure superimposed on the normal basalt spectrum. SEM examination showed the basalt particles were surrounded by a fine-grained intergranular material which gave a KEVEX spectrum indicative of SiO_2 or possibly a mixture of SiO_2 and a small amount of an aluminum silicate.

Bentonite samples were somewhat more reactive in the static hydrothermal tests than were basalt samples. In particular, Oregon bentonite gave higher solution concentrations of Na and significantly higher Ca concentrations. Montmorillonite peaks in the x-ray spectrum of the Oregon bentonite increased in intensity with increasing exposure time to hydrothermal conditions. The Wyoming bentonite, on the other hand, was characterized by the appearance of a single, large, unidentified peak in its x-ray spectrum and a corresponding decrease in the intensity of the montmorillonite peaks with increasing exposure time under 250°C hydrothermal conditions.

Under static hydrothermal conditions, the zeolite samples also showed low reactivity in the synthetic ground water. X-ray analysis of the solids similarly showed little reactivity. However, solution concentrations resulting from the stirred

test were as much as an order of magnitude greater than the average concentrations measured for other stirred samples, and of all materials studies, the enhancement of reactivity by agitation was greater for zeolite and mixtures containing zeolite.

4.6.3 Mixtures of Materials

In general, mixtures of materials gave solution reactivities that would be expected from a linear superposition of the reactivities of the individual components. For example, mixtures containing Oregon bentonite generally gave relatively high Ca concentrations in the test solutions. An exception to this linear superposition rule was found for mixtures of bentonite and zeolite in which the Ca concentrations in solution were lower than expected, perhaps due to ion exchange between the components. A somewhat surprising result was the relatively low reactivities in solution of the cementitious mixture. The accelerated ASTM cure given to the cements before hydrothermal testing may not have been sufficient to completely cure them. Exposure to hydrothermal conditions would promote the cementing reactions that might tend to tie up ions which otherwise would leach into the test solution. Whether the leach rates would increase for longer test periods is unknown.

X-ray analysis of the solid residues of the mixtures was limited by the complexity of the spectra. However, a weak trend toward montorillonite formation was noted for mixtures containing basalt.

4.6.4 Summary

To summarize these results, all the materials studied are very stable under the specified hydrothermal test conditions.

Comparison of ionic solution concentrations for the candidate plug materials with those of stable glasses tested under less extreme hydrothermal conditions shows that candidate materials are considerably less reactive. For static hydrothermal tests, reactivities are about the same at both 150°C and 250°C. Stirring the solution has the greatest effect on increasing candidate material reactivities. In mixtures containing basalt, this reactivity leads to cementing of the powders. Commercial cements were slightly less reactive than the average material tested, indicating that they should be included for further consideration at this time.

4.7. CONCLUSIONS AND RECOMMENDATIONS

4.7.1. Preferred Materials

No marked differences in chemical reactivities among any of the materials were identified by this test program. Under the described test conditions all samples proved stable, as might be expected given the criteria used in their original selection for testing. The only exceptions might be the Oregon bentonite and, to a lesser extent, the Wyoming bentonite, which showed somewhat higher reactivities in the test solution than did other materials. The basalt showed a small degree of transformation to montmorillonite under hydrothermal conditions, and this was accelerated by agitation. In those experiments where agitation was performed, cementing apparently occurred by recrystallization of the glassy fraction in the basalt. The formation of montmorillonite and self-cementation reactions are considered beneficial and desirable results with respect to potential plug designs; these reactions would tend to enhance the ability of a plug to sorb radionuclide, to increase the strength of a plug, and also to lower its permeability with passing time.

The mixtures containing cement were surprisingly unreactive under the given test conditions. This might be due to further curing of the cements even after the standard ASTM aging treatment. The crystal growth and phase changes that occurred during cement aging may have tied up the species being analyzed, lowering their solubilities in the test solution. Whether the amount of leaching would be enhanced by much longer rest times is unknown.

In summary, the original screening procedure used to select the materials for geochemical testing included chemical stability as a major criterion. Consequently, nearly all of the materials that were tested exhibited only slight reactivities, even at elevated temperature, and tests did not show major differences among them. Such lack of distinction does not necessarily mean that all materials would be equally stable over millennia, but simply means that a 3-month test may be too short to reveal differences that may exist. Therefore, the geochemical tests do not rule out any of the candidate materials, and all materials appear to be suitable for further study and potential use in plug designs based on the test results. The self-cementing action of agitated basalt samples is considered a positive, beneficial result, which could enhance its performance in potential plug designs.

4.7.2. Future Work

Candidate plug materials will need to be subjected to more extensive geochemical testing to determine their overall suitability in advanced plug designs. The present data allow only limited predictions of possible long-term chemical stability and durability of plugs constructed from the materials discussed here; nor are they sensitive enough to

discriminate between the chemical stabilities of materials with nearly equal reactivities. Longer term experiments are needed, perhaps at slightly higher temperatures (temperatures that would accelerate reaction rates but would not exceed the thermal stability limits of the test materials) and with agitation to also provide a greater acceleration of reaction rates. Ideally, the mechanisms for plug degradation should be modeled mathematically and the model used as a guide in designing the experimental program. The data obtained from those experiments would then be put back into the model to attempt predictions of plug durability for periods of thousands of years.

One unanticipated result of these tests was the observation that powdered basalt and mixtures containing powdered basalt are rapidly self-cementing under stirred, hydrothermal conditions at 250°C. This raises the prospect of designing plug systems in which basalt is the principal plug material. Such systems are conceptually appealing because, in principle, the compositional and structural discontinuity produced by a borehole in basalt could be eliminated. Much more work needs to be done to study the factors that control basalt self-cementing, so that the feasibility of designing such a plug system can be determined. The effects of such variables as particle size, temperature, solid-water ratio, solution chemistry, pH, and stirring rate on cementing reaction also need to be analyzed. Once the reaction is understood, bulk specimens can be produced, and their physical and mechanical properties can be determined for use in calculations leading to final plug design.

5 PHYSICAL TESTING PROGRAM

5.1 INTRODUCTION

The physical testing program was designed: (1) to help select individual materials and mixtures from the list of preferred candidate materials (presented by Taylor and others, 1979; and confirmed by the work described in Chapter 3 and Table I of this report) for further testing and use in preconceptual design schemes to plug boreholes, shafts, and tunnels leading to a repository in basalt; and (2) to provide quantitative experimental data on the thermomechanical response of selected mixtures under simulated repository conditions. Candidate materials for physical testing included natural cohesive and non-cohesive granular earth materials, portland cements, hydro-thermal cements, and some standard cement additives (see Chapter 4, Section 4.2). These materials are the same as those tested during the concurrent geochemical testing program, and Table IV presents a detailed listing of the various individual materials used in both testing programs. Various aspects of the physical testing program required different proportions of components in various test mixtures and different sample and particle sizes from the geochemical testing program. These variations in sample design for physical testing are discussed at appropriate intervals in the following sections.

For the purpose of the physical testing program, mixtures made from the candidate materials listed in Table IV are classified into three main generic categories: (1) cementitious mixtures; (2) compacted natural earth materials; and (3) clay slurries. These mixtures were tested in two phases during this program. During an initial phase of screening tests, all preferred candidate materials and mixtures that fell into one of the

three generic categories were examined, and the most promising mixtures were selected for further examination in the subsequent phase of the program--preliminary tests. During the preliminary tests, specific, promising candidate materials and mixtures selected by the screening phase were examined in greater detail. In this chapter, the screening tests are described for cementitious mixtures (Section 5.2), compacted earth materials (Section 5.3), and clay slurries (Section 5.4). The following sections (5.5 to 5.7) discuss the parallel, preliminary tests for these categories of materials. Final sections in the chapter provide a summary (Section 5.8) and conclusions and recommendations (Section 5.9).

5.2 CEMENTITIOUS MIXTURES - SCREENING TESTS

5.2.1 Background

Candidate cementitious mixtures for plugging man-made accesses to a repository in basalt should be characterized by good working ability, low permeability, good bonding properties, and long-term integrity and durability. In related research, portland cements were recommended by Eilers and Spangle (1973) as the primary sealant for boreholes because of portland cement's "proven permanence, low porosity, and good bond strength to formation material." Preferred portland cements included Types II and V because of sulfate resistance, and Chem Com expanding cements because of their ability to provide a compressive self-stressing effect against confining walls, thus resulting in a higher bond strength to formation material. The best performing Chem Com cement was reported to be El Toro Chem Com from Southwestern Portland Cement Company; this cement is no longer available. TXI Chem Com made by Texas Industries was

considered next best in performance characteristics, and it was evaluated in this study.

Boa (1978) included fly ash and natural high silica pozzolans in his selection of candidate grouts for plugging. These additives improve the impermeability of cement mixtures, and the addition of natural or artificial pozzolan in mixtures should also reduce bleeding and segregation, lower the heat of hydration and thermal shrinkage, and improve chemical resistance and long-term integrity and durability of the cementitious material. In this study, preference is given to natural, high-silica pozzolan because of its documented history of survival. In addition, natural high-silica pozzolan has been found to provide cementitious mixtures that have greater sulfate resistance than fly ash (Mather, 1977). Accordingly, this study includes: (1) premixed portland pozzolan cement containing 15 percent (by weight) expanded shale; and (2) a natural calcined, high-silica volcanic ash (Lassenite), which was added to various cement mixtures during the batching process.

To improve workability of fresh grout or concrete, several additives were used. One additive (Plastiment) was a water-reducing retarder agent (WRA) which, when introduced in very small quantities, causes a reduction of the required water and provided a stronger, denser product. Another additive was small amounts of finely ground aluminum powder which reacted with the alkaline constituents of portland cement to produce hydrogen gas. This resulted in an early expansion of cementitious mixtures prior to setting and improved the contact of fresh cement mixtures against irregular surfaces.

Cement mixtures to be placed near the waste repository should also have enough thermal stability to withstand cyclic temperature increases caused by the storage of radioactive wastes. Conventional portland cement mixtures are reported to be unstable at elevated temperatures (Roy and others, 1976). Under elevated pressure and temperature conditions, the original highly cementitious calcium silicate hydrates into crystalline calcium oxide (lime) that has lower strength and higher permeability. A feasibility study by Roy and others (1976) on hydrothermal transport indicated that the addition of finely ground silica flour to conventional portland cement produces a thermodynamically stable phase, tobermorite, which results in a denser, stronger final product. To minimize deterioration of cement mixtures at elevated temperature, the following two alternatives were examined during this phase of the testing program: (1) the addition of finely ground silica to portland cements (both a -325 mesh silica flour and a high silica pozzolan); and (2) the use of calcium aluminate cements (Fondu and Secar). In the second case, the main component is calcium aluminate as distinguished from calcium silicate in portland cements; no free lime is liberated either during hydration or heat exposure in calcium aluminate cements. Fine and coarse aggregates used in all cement mixtures were chosen for their ready availability and proximity to the Hanford Site; they include crushed and naturally graded sands and gravels and crushed basalt.

5.2.2 Materials and Mixtures Used in Cements

Candidate materials in cement mixtures and the source of each material are listed in Table VII. The combination of components used in each mixture and data on the relative proportion of each component in a mixture are summarized in

TABLE VII

CANDIDATE MATERIALS USED IN SCREENING TESTS ON CEMENT MIXTURES

Material	Source
Portland Type V cement	Kaiser Cement
Portland Type II cement	Portland Oregon Cement
Portland pozzolan cement	Kaiser Cement
Fondu (calcium aluminate cement)	Lone Star Lafarge
Secar (calcium aluminate cement)	Lone Star Lafarge
TXI Chem Com cement	Texas Industries, Inc.
Glaciofluvial sand	Hanford Site
Crushed basalt	Hanford Site
Crushed zeolite	Teaque Mineral Industries
Lassenite ^a	Lassenite Industries
Silica flour (-325 mesh)	Ottawa Sand Company
Unpolished aluminum powder (-325 mesh and -200 to +325 mesh)	Valimet
Polished, leafing-type aluminum power (-325 mesh)	U.S. Bronze Powders, Inc.
Plastiment ^b	Sika Chemical Corp.
^a Calcined, natural pozzolan including tuff and diatomite. ^b Water-reducing, retarding agent (hydroxylated carboxylic acid).	

Table VIII for 22 cement mixtures. To simplify the screening process of candidate cements, the following guidelines were applied to each mixture, based on published standards and previous research:

- The water/cement ratio was selected to produce cement mortars of normal consistency, as determined at the flow table (ASTM, 1973);
- The ratio of aggregate (sand plus silica) to cement (cement plus pozzolan) was 2.5:1 (2.5 parts aggregate to 1 part cement), based on ASTM C109, adjusted;
- The ratio of silica to silica plus cement was equal to 0.35:1, based on work by Eilers and Spangle (1973);
- The ratio of pozzolan to cement was equal to 0.20:1, a standard practice, and
- The addition of 90 ml of Plastiment per bag of cement (weighing 42.6 kg) was made when a WRA was used in test mixtures, in accordance with general practice.

5.2.3 Testing Program and Procedures

Screening tests for cementitious materials included:

- The determination of unit weight, specific gravity, percentage of absorption, grain size distribution, and inorganic impurities content for candidate sands;
- The consistency and setting time of freshly mixed cementitious mixtures;

TABLE VIII

COMPONENTS AND PROPORTIONING DATA FOR CANDIDATE CEMENTITIOUS MIXTURES

MIXTURE NUMBER	PORTLAND TYPE V (g)	PORTLAND TYPE II (g)	PORTLAND POZZOLAN (g)	TXI CEMENT (g)	FONDU CEMENT (g)	SECAR CEMENT (g)	GLACIO- FLUVIAL SAND (g)	CRUSHED BASALT (g)	CRUSHED ZEOLITE (g)	SILICA FLOUR -325 MESH (g)	LAS- SENITE (g)	AL POWDER (g)	PLASTI- MENT (ml)	WATER (ml)	FLOW (%)
612					500		1250							200	115
613						500	1250							260	113
614	500						980			269				286	115
615			500				981			269				278	111
616				500			1250							235	116
617			500					981		269				278	110
618			500						981	269				676	112
619	416						1250				84			243	105
620				416			1250				84		0.98	249	104
621	500						981			269				246	113
622	416						1250				84	0.2346	0.82	223	106
623	500						981			269		0.2346	0.98	250	117
624		416					1250				84			246	106
625			500				1250							227	105

MIXTURE NUMBER	PORTLAND TYPE V (g)	PORTLAND POZZOLAN (g)	GLACIO FLUVIAL SAND (g)	ALUMINIUM POWDER -325 MESH (g)	ALUMINIUM POWDER 200/325 MESH (g)	WATER (ml)	FLOW (%)
601	500		1250			222	107
602	494		1250		0.117	221	110
603	494		1250	0.117		215	114
604	494		1250	0.2346		228	105
605	494		1250		0.2346	228	107
606	491		1250		0.3519	228	103
607	491		1250	0.3519		231	115
608		494	1250	0.2346		227	106

- The early volume change and the restrained shrinkage or expansion of candidate mixtures; and
- The unconfined compressive strength at 7 days and 28 days of hardened 5-cm cubes of cement mortar, cured using one of the methods presented in Table IX.

The procedures used during physical testing included the ASTM and the Army Corps of Engineers standards and modified standard procedures, as described in the Quality Assurance program. The list of procedures is given in Table X, and procedures on file in the Quality Assurance program, for which no literature citation exists, are briefly discussed in the text.

5.2.4 Discussion of Screening Tests on Cementitious Mixtures

5.2.4.1 The Effect of Temperature on the Compressive Strength of Cement Mortars

Comparison of strength data for samples cured at ambient temperature, 100°C, and 200°C are plotted in Figure 7 (a and b). Curing procedures for all samples are given in Table IX. There is a difference among samples for curing and testing at the ambient (23°C) temperature. For example, Fondu and Secar samples follow Procedure A (2) requiring 7 days in the mold before removing and immediate testing. Other cement samples are removed in 24 hours and tested at 28 days. The reason is in the high early strength characteristics of Fondu and Secar cements. Curing for elevated temperature tests was the same for all samples and is given in Table IX (B). All elevated temperature testing was at 28 days.

TABLE IX

CEMENT CURING PROCEDURES

- A. Wet-curing at standard temperature (23°C)
- (1) For non-expansive or quick-hardened, cement mortars, specimen wet-cured 24 hours within the mold, then removed and cured in a moist room before testing.
 - (2) For expansive cement mortar, specimen wet-cured 7 days within the mold, then removed and cured in a moist room before testing.
- B. Wet-curing at elevated temperature, initial curing for 24 hours within the mold followed by one of the following curing alternatives:
- (1) In boiling water for 72 hours at 100°C.
 - (2) In an autoclave for 72 hours at 200°C.

TABLE X

TESTING PROCEDURES APPLIED TO CEMENTITIOUS MIXTURES

ASTM C-29 ^a	Unit weight of aggregate
ASTM C-128 ^a	Specific gravity and absorption of fine aggregate
ASTM C-40 ^a	Inorganic impurities
ASTM D-422 ^b	Particle size analysis of soil
ASTM C-230 ^a	Specification for flow table for use in test of hydraulic cement
ASTM C-191 ^c	Setting time by Vicat needle
ASTM C-827 ^a	Early volume change of cementitious mixtures
CRD C-588 ^d	Restrained expansion of cement mortars: Corps of Engineers method
Modified ASTM C-109 ^a	(1) Compressive strength of expansive or shrinkage- compensating cement mortars. (2) Compressive strength of non-expansive and rapid- hardening cement mortars. (3) Effect of heat exposure on the compressive strength of wet cement mortars. Modifications include variations in curing procedures described in the text.

^aASTM (1977b)^bASTM (1978b)^cASTM (1973)^dU.S. Army Corps of Engineers (1978)

FIGURE 7

COMPRESSIVE STRENGTH OF CEMENT MORTAR MIXTURES
AT ELEVATED CURING TEMPERATURES

Descriptions of the mixture components, water/cement ratios, setting times, and compressive strengths are summarized in Table XI. Corresponding mixture descriptions, water/cement ratios, setting times, and shrinkage/expansion characteristics are given in Table XII.

Prior to discussing Figure 7, it is useful to note that (1) property changes observed in specimens heated under a confined free moisture condition are primarily related to changes in the mineralogy of the cementitious phase (Lankard and others, 1970); and (2) the percent strength retained by portland cement (without additives and after autoclaving) has been observed to range from 76 percent at 115°C to 29 percent at 199°C (Akaiwa and Sudoh, 1966). The following results were considered most important for this screening phase of cementitious mortar mixtures with respect to temperature effects:

- TXI Chem Com (shrinkage compensating cement) showed a decrease in strength with increasing curing temperature. The addition of Lassenite to the mixture slightly increased the strength of the cementitious mixture, but the percent deterioration with temperature increase remained the same. Strength percent remaining after autoclaving ranged from 65 percent at 100°C to 35 percent at 200°C (Figure 7a);
- Portland pozzolan cement remained quite stable for curing temperatures less than 100°C but underwent a net strength decrease when cured at higher temperatures (Figure 7a);
- The addition of 20 percent Lassenite (by weight of cement) in mixtures of portland cement Type V stabilized the structural properties of the mixture. Therefore, no

TABLE XI
SUMMARY OF TEST RESULTS FOR CEMENT MORTARS
CURED AT ELEVATED TEMPERATURE

MIXTURE NUMBER	CEMENT DESCRIPTION	SAND DESCRIPTION	ADDITIVE DESCRIPTION	WATER CEMENT RATIO		SETTING TIME		UNCONFINED STRENGTH (MPa)	
				W/C	W/C+ SILICA	INITIAL	FINAL	CURING AT t = 100°C	CURING AT t = 200°C
612	FONDU	GLACIOFLUVIAL SAND	NA*	0.40	NA	2:00	3:30	33.9	24.6
613	SECAR	GLACIOFLUVIAL SAND	NA	0.51	NA	1:40	2:50	32.4	35.6
614	PORTLAND TYPE V	GLACIOFLUVIAL SAND	SILICA FLOUR	0.57	0.37	2:45	4:00	50.1	106.1
615	PORTLAND POZZOLAN	GLACIOFLUVIAL SAND	SILICA FLOUR	0.56	0.36	2:15	3:45	53.3	101.7
616	TXI	GLACIOFLUVIAL SAND	NA	0.47	NA	1:40	3:35	38.3	16.7
619	PORTLAND TYPE V + LASSENITE	GLACIOFLUVIAL SAND	NA	0.49	NA	3:15	5:15	48.3	47.8
620	TXI + LASSENITE	GLACIOFLUVIAL SAND	NA	0.50	NA	1:30	3:45	43.6	22.2
621	PORTLAND TYPE V	GLACIOFLUVIAL SAND	SILICA FLOUR + PLASTIMENT	0.49	0.32	3:00	6:30	53.0	116.3
622	PORTLAND TYPE V + LASSENITE	GLACIOFLUVIAL SAND	PLASTIMENT	0.45	NA			56.1	53.2
623	PORTLAND TYPE V	GLACIOFLUVIAL SAND	SILICA FLOUR + PLASTIMENT + AL POWDER	0.50	0.33			58.5	111
624	PORTLAND TYPE II + LASSENITE	GLACIOFLUVIAL SAND	NA	0.53	NA	1:50	4:20	40.6	31.8
625	PORTLAND POZZOLAN	GLACIOFLUVIAL SAND	NA	0.45	NA			60.9	33.1

*Not applicable

TABLE XII

SUMMARY OF TEST RESULTS FOR CALCIUM ALUMINATE CEMENT MORTARS

MIXTURE NUMBER	COMPONENTS DESCRIPTION	ADDITIVE DESCRIPTION	WATER/ CEMENT RATIO W/C	SETTING TIME		MAXIMUM EARLY VOLUME CHANGE	RESTRAINED VOL. CHANGE		UNCONFINED COMPRESSION	
				INITIAL hr:mn	FINAL hr:mn		3 days	7 days	24 hours	7 days
612	FONDU CEMENT/ GLACIOFLUVIAL SAND	NONE	0.40	2:00	3:30	-0.11	-0.02	-0.03	47.6	56.2
613	SECAR CEMENT/ GLACIOFLUVIAL SAND	NONE	0.52	2:50	2:50	-0.05	0.00	+0.02	30.5	37.3

decrease in strength was observed between a specimen cured at 100°C and a specimen cured at 200°C (Figure 7a);

- No such strength stabilization was observed in the mixture which included portland cement Type II plus Lassenite, where a 20-percent decrease in strength was observed between specimens cured at 100°C and at 200°C (Figure 7a);
- The calcium aluminate cement, Fondu, underwent a substantial decrease in strength when cured at elevated temperatures (Figure 7b);
- The calcium aluminate cement, Secar, appeared to be quite stable, and no significant change in strength was observed between a specimen cured in a moist room at ambient temperature and specimens cured at 100°C and 200°C. However, the strength of a cement mixture fabricated with Secar was lower than the strength of a mixture made from portland cement when specimens cured at ambient temperature were compared (Figure 7b);
- The addition of 35 percent finely ground silica flour (by weight of cement plus silica) caused a strong hydrothermal reaction that greatly improved the structural strength of portland cement Type V cured at elevated temperatures. Specimens containing silica flour and cured at 200°C developed a compressive strength twice as great as the same material cured at 100°C. This result is noteworthy considering that portland cement without a silica additive showed a three-fold decrease in strength when submitted to the same comparative test (Figure 7b); and

- Mixtures of portland pozzolan cement containing silica flour showed the same behavior as mixtures of portland cement Type V plus silica flour, and structural strengths developed during the curing process were similar for the two cement types when silica was present (Figure 7b).

5.2.4.2 The Effect of Aluminum Powder on Portland Cement Mixtures

Table XIII summarizes test data (including water/cement ratios, setting times, maximum early volume changes, restrained volume changes, and 7-day and 28-day compressive strengths) for portland cements mixed with fine-grained, unpolished aluminum powders. Both -325 mesh and -200 to +325 mesh unpolished aluminum powder were tested in cement mixtures in quantities ranging from 0.023 to 0.070 percent by weight of the cementitious materials. Figure 8 (a and b) presents data on the variation in compressive strength (at 7 and 28 days) and in restrained shrinkage for increasing unpolished aluminum powder/cement ratios. The following observations were made with respect to increasing aluminum powder contents in cement mixtures:

- An increase in the water/cement ratio was necessary to obtain the same workability. This resulted in an increase in porosity of the cement mixture;
- There was a notable acceleration of setting times;
- Restrained shrinkage continuously decreased with increasing content of -325 mesh aluminum powder, which resulted in a non-shrink mortar for the largest aluminum powder content (0.070 percent) studied (Figure 8b);

TABLE XIII

SUMMARY OF TEST RESULTS FOR PORTLAND CEMENT MORTARS
CONTAINING UNPOLISHED ALUMINUM POWDER

MIXTURE NUMBER	COMPONENTS DESCRIPTION	ADDITIVE DESCRIPTION (Weight %)	WATER/ CEMENT RATIO W/C	SETTING TIME		MAXIMUM EARLY VOLUME CHANGE	RESTRAINED VOL. CHANGE		UNCONFINED COMPRESSION	
				INITIAL hr:mn	FINAL hr:mn		3 days	7 days	7 days	28 days
601	PORTLAND TYPE V/GLACIO- FLUVIAL SAND	NONE	0.44	2:54	5:32	-0.40%	-0.55%	-0.57%	38.1	48.5
602	PORTLAND TYPE V/GLACIO- FLUVIAL SAND	AL POWDER -200/+325 MESH 0.023 %	0.43	2:00	3:15	-0.34%	-0.05%	-0.05%	45.7	49.3
603	PORTLAND TYPE V/GLACIO- FLUVIAL SAND	AL POWDER -325 MESH 0.023 %	0.44	2:18	4:20	-0.46%	-0.23%	-0.24%	41.1	51.9
604	PORTLAND TYPE V/GLACIO- FLUVIAL SAND	AL POWDER -325 MESH 0.047 %	0.46	2:05	3:15	-0.29%	-0.05%	-0.05%	37.2	49.6
605	PORTLAND TYPE V/GLACIO- FLUVIAL SAND	AL POWDER -200/+325 MESH 0.047 %	0.46	2:10	4:00	-0.50%	-0.13%	-0.15%	36	53.8
606	PORTLAND TYPE V/GLACIO- FLUVIAL SAND	AL POWDER -200/+325 MESH 0.070%	0.47	2:00	3:00	-0.34%	-0.32%	-0.29%	36.8	52.4
607	PORTLAND TYPE V/GLACIO- FLUVIAL SAND	AL POWDER -325 MESH 0.070%	0.46	2:20	3:45	-0.32%	0.00	0.00	38.3	50.7
608	PORTLAND POZZOLAN/ GLACIO- FLUVIAL SAND	AL POWDER -325 MESH 0.023%	0.46	2:00	3:45	-0.71%	+0.02%	+0.02%	42.1	64.5

a) Effect of aluminum powder on the compressive strength of wet cement mortars

b) Effect of aluminum powder on the early volume change of wet cement mortars

EXPLANATION

- -325 mesh unpolished aluminum powder
- -200/+325 mesh unpolished aluminum powder

FIGURE 8

EFFECT OF ALUMINUM POWDER ON THE
STRENGTH AND VOLUME CHANGE PROPERTIES OF WET CEMENT MORTARS

- An optimum, restrained shrinkage reduction was observed for samples containing 0.023 percent aluminum powder using the -200/+325 mesh grain size. An increase in shrinkage was observed with further additions of aluminum powder with this grain size (Figure 8b); and
- No substantial changes in the compressive strength of cement specimens occurred with increasing powder content; at equal water/cement ratios, a slight increase in strength was noted (Figure 8a).

Cement mixtures containing portland pozzolan cement and 0.023 percent -325 mesh unpolished aluminum powder were slightly expansive. The strength of a 28-day, moist-cured specimen of portland pozzolan cement was observed to be 30 percent higher than the strength of a specimen fabricated from portland cement Type V.

Those data on early volume changes produced by the addition of unpolished aluminum powders are difficult to interpret and somewhat contradictory. An expected early expansion of cement mortars (due to the reaction of aluminum powder with alkaline solutions) was not observed, even when using twice the amount of aluminum powder generally recommended (U.S. Bureau of Reclamation, 1975). This lack of expansion suggests that the commercial-grade unpolished aluminum powder used in these tests was poorly suited to react with the cement mixtures as a gas-forming agent.

A -325 mesh polished, leafing-type aluminum powder was also investigated. The reactivity of this aluminum powder was determined by measuring the change in volume of a grout column

from its original height and its height at the end of a specified period, following the C-681 standard method (U.S. Army Corps of Engineers, 1978). (The proportions of components used in grout mixtures during this part of the screening tests are presented in Section 5.4.) Cement grouts used in comparing the relative reactivities of -325 mesh unpolished aluminum powder and -325 mesh polished, leafing-type aluminum powder were designed with identical components, and the proportions of those components (portland cement Type V, Lassenite, and glaciofluvial sand) were designed to provide the same flow, as determined with a Marsh funnel. Curves giving the early volume change of fresh grout per time elapsed for a control mixture without aluminum powder, a mixture containing 0.048 percent by weight of -325 mesh unpolished aluminum powder, and a mixture containing 0.048 percent by weight of -325 mesh polished, leafing-type aluminum powder are presented in Figure 9. These curves indicate a considerable difference in reactivity between the two grades of aluminum powder. Fresh grout with unpolished aluminum powder exhibited shrinkage of 0.068 percent. However, the grout with polished, leafing-type aluminum powder exhibited a strong, unrestrained expansion, reaching 14 percent in 4 hours. A study of the optimum content of polished, leafing-type aluminum powder (the results of which are presented in Figure 10) resulted in the selection of 0.03 percent aluminum powder in cement mixtures by weight, which produced about 8 percent of pre-expansion before set of the mixture.

5.2.4.3 The Effect of a Water-Reducing Retarder Agent (WRA) on Portland Cement Mixtures

Although organic components in cement mixtures may have a poorly documented history of survival and durability, their use in small amounts may prove to be highly desirable. Their

FIGURE 9

THE EFFECT OF TWO TYPES OF ALUMINUM POWDER ON
THE EXPANSION CHARACTERISTICS OF FRESH GROUTS

FIGURE 10

**THE EFFECT OF INCREASING THE CONTENT OF A -325 MESH
POLISHED, LEAFING-TYPE ALUMINUM POWDER ON
THE EXPANSION CHARACTERISTICS OF FRESH GROUT**

addition to cement mortars improves plasticity, decreases mixing water requirements, lengthens the time of set, and avoids flash setting in moderate to high temperature environments. The thermal stability of cementitious mixtures containing a WRA, Plastiment, was examined during unconfined compressive strength tests on 5-cm cement cubes cured in an autoclave at 100°C and 200°C. A description of the mixtures, water/cement ratios, setting times, and strengths is presented in Table XI.

Strength values are plotted on Figure 11 for cement mortars containing portland cement Type V plus Lassenite and portland cement Type V plus silica flour. For both of these mixtures, the addition of 90 ml of Plastiment per bag of cement (42.6 kg) slightly increased the strength of mortars cured at elevated temperature. Comparative values of compressive strengths for mortars containing portland cement Type V plus Lassenite indicated a strength increase reaching 18 percent for a specimen cured at 100°C and 11 percent for a specimen cured at 200°C (with Plastiment added). For mixtures containing portland cement Type V plus silica flour, the strength increase reached 6 percent for a specimen cured at 100°C and 10 percent for a specimen cured at 200°C.

Strength tests were also performed on mixtures of portland cement Type V plus silica flour which contained both Plastiment and aluminum powder. Data plotted on Figure 11 show a slight increase in strength. Comparative values of strength obtained for mixtures containing both Plastiment and aluminum powder versus mixtures containing only Plastiment indicated a 10 percent gain in strength for a specimen cured at 100°C and a 5 percent loss in strength for a specimen cured at 200°C. These percentages of gain and loss are relatively small and are

EXPLANATION

- Plain mixture
- Mixture includes WRA
- △ Mixture includes aluminum powder and WRA

FIGURE 11

COMPRESSIVE STRENGTH OF CEMENT MIXTURES
CONTAINING A WRA (PLASTIMENT) AND ALUMINUM POWDER
AT ELEVATED CURING TEMPERATURES.

within the range of accuracy to be expected from experimental strength values. Thus, no firm conclusion can be reached as to the effect of a WRA on strength.

5.2.4.4 Performance of Candidate Sands

Figure 12a gives values of unit weight, specific gravity, percentage of absorption, and inorganic impurities of glaciofluvial sand, crushed basalt, and crushed zeolite. Figure 12b gives the grain size distribution curves of these three candidate sands relative to two grading limit curves proposed by ASTM C-33 (ASTM, 1977b) for sand used in mortar and concrete. The basalt and zeolite sands had to be crushed to conform to ASTM requirements. The glaciofluvial sand and the crushed-basalt sand have similar physical properties and are recommended for cement mixtures. Crushed zeolite appears to be a porous, weak aggregate. A large amount of breakdown was observed during blending of this material.

Comparative values for water/cement ratios and compressive strengths, together with mixture designs, are given in Table XIV. Three cement mixtures were cured at 100°C and at 200°C using the same cements and additives but containing different aggregates. Experimental strength values are plotted on Figure 13. Cement mortars mixed with glaciofluvial sand and crushed basalt developed similar strengths. Cement mortar mixed with crushed zeolite had an extremely weak structural strength. The amount of water used with crushed zeolite aggregate to maintain the same consistency was twice that used for either crushed basalt or glaciofluvial sand. This demand for water and weak strength suggests a porous cement mortar.

(a)

SAMPLE NUMBER	DESCRIPTION	UNIT WEIGHT (Kg/m ³)	SPECIFIC GRAVITY	ABSORPTION	INORGANIC IMPURITY
A-79	GLACIOFLUVIAL SAND	1824.5	2.75	1.83%	NONE
A-82-SAND-R	CRUSHED BASALT	1853.3	2.96	2.33%	NONE
A-59-R	CRUSHED ZEOLITE	981.5	1.73	34.3%	NONE

(b)

FIGURE 12
INDEX PROPERTIES OF CANDIDATE SANDS

TABLE XIV

SUMMARY OF TEST RESULTS FOR PORTLAND POZZOLAN CEMENT MORTARS
CONTAINING DIFFERENT AGGREGATE TYPES

MIXTURE NUMBER BBPP-PT	COMPONENTS DESCRIPTION	ADDITIVE DESCRIPTION	WATER CEMENT RATIO		UNCONFINED COMPRESSION (MPa)	
			W/C	W/C + SILICA	BOILING WATER CURING 100°C	AUTOCLAVE 200°C
615	PORTLAND POZZOLAN/ GLACIOFLUVIAL SAND	SILICA FLOUR	0.56	0.36	53.3	101.7
617	PORTLAND POZZOLAN/ CRUSHED BASALT	SILICA FLOUR	0.56	0.36	54.3	98.1
618	PORTLAND POZZOLAN/ CRUSHED ZEOLITE	SILICA FLOUR	1.39	0.88	14.9	21.7

FIGURE 13

PERFORMANCE OF CEMENT MIXTURES CONTAINING PORTLAND TYPE V, SILICA FLOUR, AND THREE TYPES OF FINE AGGREGATE

5.2.5 Results of Screening Tests on Cementitious Mixtures

Calcium aluminate cement (Fondu), portland pozzolan cement, portland cement Type II with a natural pozzolan added, and TXI Chem Com cement (with or without pozzolan) show a substantial deterioration in structural strength when subjected to elevated temperature.

Portland cement Type V mixed with a high-silica pozzolan (Lassenite) and Secar cement are stable and exhibit no significant change in strength with increasing curing temperature. However, strengths developed by mixtures of portland cement Type V plus Lassenite are about 35 percent higher than strengths developed by mixtures of Secar cement. On the basis of data indicating high structural strength, the addition of finely ground silica powder to portland cements appears to be highly desirable in mixtures designed for use in high-temperature (greater than 100°C) plug locations.

Large variations in reactivity were observed between the various grades of aluminum powder tested in this program. Whereas 0.070 percent -325 mesh unpolished aluminum powder by weight of cement was necessary to eliminate early shrinkage in portland cement Type V mixtures, 0.03 percent of -325 polished, leafing-type aluminum powder was found to produce 8 percent free expansion in cement mixtures. Initial testing of cement mortars containing unpolished aluminum powder indicated that, for the same consistency, an increase in the aluminum powder ratio required: (1) an increase in the water/cement ratio (thus causing increased bleeding and segregation and a less dense mortar); and (2) an acceleration of the set of the mixture. The use of a WRA, Plastiment, which can reduce the amount of water required for a given cement consistency and

also retard the rate of stiffening, is expected to improve significantly the expansive characteristics and structural behavior of mixtures containing aluminum powder. Experimental compressive strength values for specimens, which were cured at elevated temperatures and which contain both a WRA and aluminum powder, indicated that no additional deterioration was caused by either the addition of a WRA or aluminum powder. On the contrary, there was a slight increase in structural strength. The use of crushed zeolite in cement is not desirable, based on low strength results and high water demand for a given consistency. The results of tests on mortars made with either glaciofluvial or crushed basalt were similar and indicate a strong, dense, competent material.

5.3 COMPACTED EARTH MATERIALS - SCREENING TESTS

5.3.1 Background

The feasibility of using compacted earth materials to plug boreholes has been examined by Martin (1975) for shale and montmorillonite/quartz sand mixtures. Buffer materials composed of quartz sand and bentonite and highly compressed bentonite blocks have been proposed by workers in Sweden (Swedish Nuclear Fuel Safety Project, 1979) to seal canister storage holes. In addition to blocking radioactive waste migration in ground water, compacted sandy clay mixtures are expected to provide ion exchange and sorption capabilities to help retard the migration of radionuclides through the plug system in two other ways.

In preliminary physical testing, emphasis was placed on materials readily available in the proximity of the Hanford Site. Compacted earth materials used in plugs should combine

low permeability with low compressibility, have a high shear strength, and form a good bond with surrounding rocks. In a sand/clay mixture, impermeability is provided by the clay fraction while low compressibility and high shear strength are obtained by increasing the sand fraction. However, the addition of too much sand will affect the impermeability of the mixture. Preliminary screening tests were designed to evaluate the values and the sensitivity of selected mechanical properties (permeability and strength) to various sand/clay ratios, in order to select optimum mixtures for later testing of hydraulic properties.

5.3.2 Candidate Earth Materials and Mixtures

Compacted earth materials evaluated during the screening test phase and the sources for these materials are listed in Table XV. Samples for testing included mixtures of clays and glaciofluvial sand (in order to examine the properties of different clay/sand ratios) and skip-graded, coarse-crushed basalt in clay/sand mixtures (to ascertain the effect of a coarse aggregate on mixtures of fine-grained materials).

5.3.3 Testing Program and Procedures

Screening tests for compacted natural materials included:

- Grain size analysis, specific gravity, and relative density of non-cohesive granular materials;
- Grain size analysis, specific gravity, and Atterberg limits on clays;

TABLE XV

NATURAL MATERIALS USED IN SCREENING TESTS
ON COMPACTED EARTH MATERIALS

<u>Material:</u>	
<u>Seven candidate clayey soils</u>	<u>Source: Pasco Basin</u>
Oregon bentonite (-200 mesh)	Teaque Mineral Industries
Oregon bentonite (-20 to +160 mesh)	Teaque Mineral Industries
Wyoming bentonite	Baroid National Brand
Glaciofluvial sand	Hanford Site
Fine-crushed zeolite (-2.6 mm)	Teaque Mineral Industries
Fine-crushed basalt (-4.6 mm)	Hanford Site
Coarse crushed basalt (-1.9 cm)	Hanford Site

- Moisture/density relationships in mixtures after impact compaction;
- Swelling pressure under conditions of zero volume change on mixtures compacted at maximum dry density and at the optimum water content; and
- Determination of stress-strain relationships under unconfined compression for candidate mixtures compacted to the maximum dry density at the optimum water context.

The procedures used in testing compacted earth materials included both standard published procedures and special test methods developed and described in the Quality Assurance program. A list of the procedures is given in Table XVI. The special test methods that were used in this study and that have no published reference, are described in more detail here.

5.3.3.1 Maximum/Minimum Density of Non-Cohesive Granular Material

Minimum density is first determined on an oven-dried sample by pouring the sample into a cylindrical mold (7 cm in diameter by 12.7 cm in height) through a 2.5-cm diameter pouring spout of a funnel with a spiral motion from the outside toward the center until the mold is filled to overflowing capacity. The excess material is then struck off, and the weight of the material is recorded. This procedure is repeated a minimum of three times, and an average minimum density value is calculated.

The same volume mold is used to determine the maximum density. A porous stone is placed on the bottom of the mold, and the mold is filled with water to one-third of its

TABLE XVI

TESTING PROCEDURES APPLIED TO COMPACTED EARTH MATERIALS

ASTM D-422 ^a	Particle size analysis of soils
ASTM C-128 ^b	Specific gravity and absorption of fine aggregate
Special test method (see text)	Maximum/minimum density of non-cohesive granular material
ASTM D-854 ^a	Specific gravity of soils
ASTM D-423 ^a	Liquid limit of soils
ASTM D-424 ^a	Plastic limit of soils
ASTM D-427 ^a	Shrinkage factors of soils
Special test method (see text)	Moisture/density relation of soil using a 4.5-kg rammer and a 45-cm drop (tested in a 6.25-cm diameter mold)
Test method suggested by the International Society for Rock Mechanics ^c	Determination of the swelling pressure under conditions of zero volume change
ASTM D-2166 ^a	Unconfined compressive strength of cohesive soils

^aASTM (1978b)^bASTM (1977b)^cInternational Society for Rock Mechanics (1978)

capacity. The oven-dried soil is then added to fill the mold to within 3.8 cm of the top. A porous stone is placed on the upper end of the sample, and a spring is placed on the porous stone so that when the mold cap is bolted in place, there is a surcharge equivalent to 141 g/cm^2 . A vacuum of about 0.1 MPa is then applied to the lower end of the mold, and the upper end is open to the atmosphere. The mold is then vibrated at a frequency of approximately 30 impact vibrations per minute, and the energy expended is approximately $2 \text{ kilonewton-m/m}^3$ per cycle. This energy and frequency are maintained until all excess water is removed from the mold and no further reduction in height can be observed. The height and weight of the sample are recorded, and the maximum dry density is calculated after the sample is oven-dried.

5.3.3.2 Impact Compaction

A method was designed to standardize the compaction process to be used on sand/clay and sand/clay/coarse-aggregate mixtures throughout the testing program. This method is sensitive to a maximum particle diameter in a sample when testing the strength and the swelling of soil samples with standard laboratory soil testing equipment. During compaction, densification is achieved by impacting the 5-cm diameter tamper foot of a standard 4.5-kg rammer concentrically into a 6.35-cm diameter mold. Impact, height, and the number of lifts compacted in each sample are the same as for ASTM D-1557 standard procedure (ASTM, 1978b). The only difference between the two procedures is the size of the mold, which is 10.16 cm in diameter in ASTM D-1557. Comparative tests were carried out on a pure clay specimen and on a -1.9-cm coarse-crushed basalt/sand/clay mixture using both compaction methods. As shown in Figure 14, no significant difference was observed for the optimum water

EXPLANATION

- Impact compaction ASTM D-1557 in a 10.16-cm diameter mold
- Special compaction in a 6.35 - cm diameter mold

FIGURE 14

INFLUENCE OF THE MOLD DIAMETER SIZE ON IMPACT COMPACTION

content. A greater densification is obtained in the 6.35-cm diameter mold for both mixtures, and the difference in maximum dry density between the two compactive methods is greater for larger, maximum aggregate size, indicating that good, standardized compaction can be obtained on coarse aggregate mixtures.

5.3.4 Discussion of Screening Tests on Candidate Clayey Soils from near the Hanford Site

5.3.4.1 Index Tests and Field Reconnaissance

Atterberg limits were performed on representative composite samples of several fine-grained units in the Pasco Basin to provide a preliminary evaluation of the suitability of these clays as candidate cohesive materials. Criteria for this preliminary evaluation included high plasticity, good accessibility, homogeneity, and sufficient nominal thickness of the unit to assure availability in case of later use as an actual plug material (Figure 15). Atterberg limits, soil classifications, and first estimation of accessibility, homogeneity, and bulk availability of the units sampled are summarized in Figure 15c. Two clayey soils were selected as potential cohesive materials: (1) clayey soil from Unit D (Ringold clay D) because of its high plasticity combined with a satisfactory bulk availability, homogeneity, and accessibility; and (2) clayey soil from Unit C (Ringold clay C), which is of an inorganic clay of medium plasticity and moderate compressibility.

(a) Descriptive evaluation of bulk availability, homogeneity, and accessibility

LITHOLOGY AT RINGOLD FLAT-PARSON CANYON SECTION

(b) Plasticity evaluation

(c) Ringold clayey soil sample selection

Sample Number	Unit (i.e., lithology)	Liquid Limit	Plastic Limit	Plastic Index	Soil Classification	Availability Accessibility Homogeneity
A-62	A	62.2	23.6	38.6	CH	slight
A-63	B	27.6	24.2	3.4	ML	fair
A-64	C	44.6	25.8	18.8	CL	good
A-66	D	63.9	23.1	40.8	CH	good
A-67	E	112.5	44.6	67.9	MH-CH	questionable
A-68	F		NON - PLASTIC			slight
A-69	Touchet Formation (TOU)	22.9	22.4	0.5	ML	good

FIGURE 15

SELECTION CRITERIA AND DATA RESULTS
FOR THE CANDIDATE RINGOLD CLAYEY SOILS

5.3.4.2 Mechanical Properties

Compaction tests and unconfined compression tests were carried out on Ringold clays C and D (Figure 16). The compaction curves (Figure 16a) indicated that slightly higher densification was obtained on Ringold clay D, although a low maximum dry density was observed ($1,650 \text{ kg/m}^3$), indicating poor compactibility for this material. Unconfined compression curves (Figure 16b) for the two clay materials also showed that Ringold clay D has higher strength and stiffness. The high optimum water content suggests further potential difficulty when using standard field compaction methods. An alternative candidate material is produced by mixing Ringold clay with sand, thus reducing the amount of water required and increasing the dry density. However, field mixing of Ringold clay with sand would probably be somewhat difficult and costly.

In conclusion, Ringold clay D was selected for further testing based on index test data, geological reconnaissance, and its mechanical properties. The screening process compared the performances of selected samples from near the Hanford Site in the Pasco Basin, and Ringold clay D was considered to perform best of those cohesive soil materials screened. Although Ringold clay D may have potential use as a plug material when compared with clayey soils from other regions, this material was not considered exceptional because of its high silt content, high shrinkage limit, and relatively low maximum dry density after compaction.

(a) Compaction curves for candidate Ringold clays

(b) Unconfined compressive strength curves for candidate Ringold clays

FIGURE 16
MECHANICAL BEHAVIOR OF CANDIDATE RINGOLD CLAYS

5.3.5 Discussion of Screening Test on Candidate Non-Cohesive Granular Materials

Grain size distributions of candidate non-cohesive granular materials are presented in Figures 12 and 17. Table XVII gives the index properties of these materials. As was discussed in Section 5.2.4.4, crushed basalt and glaciofluvial sand have the properties of strong and competent aggregates. If used in compacted backfill, they will provide structural strength and volumetric stability. By contrast, crushed zeolite has a low unit weight, low specific gravity, and high porosity. Breakdown was observed during the blending of composite zeolite samples. Because of the high ion exchange and sorption capacity of crushed zeolite, it will be retained for consideration as a candidate material to improve the performance of compacted backfill in inhibiting radionuclide migration. Crushed basalt and glaciofluvial sand remain the preferred candidates for use as aggregates in compacted cohesive mixtures in potential plugs.

5.3.6 Discussion of Screening Tests on the Index Properties of Candidate Clays

Tests were performed to determine the index properties of four candidate clays: two Oregon bentonites; one Wyoming bentonite; and Ringold clay D. Results are presented in Figure 18a. Relationships between liquid limit and plasticity index (Figure 18b) and values of activity (Figure 18c) are given for various clay minerals. In the following discussion, clay activity, as defined by Skempton (1953), is the ratio of the plasticity index to the amount of the clay fraction (defined as the percentage dry weight of the -2-mm fraction of the sample). Wyoming bentonite has a high plasticity index and

Cobbles	Gravel		Sand		
	Coarse	Fine	Coarse	Medium	Fine

FIGURE 17
GRAIN SIZE DISTRIBUTION OF THE COARSE-CRUSHED BASALT

TABLE XVII

INDEX PROPERTIES OF CANDIDATE NON-COHESIVE GRANULAR MATERIALS

MATERIAL DESCRIPTION	MAXIMUM DENSITY (kg/m ³)	MINIMUM DENSITY (kg/m ³)	GRAIN POROSITY	SPECIFIC GRAVITY
COARSE-CRUSHED BASALT	1,619.5	1,358.4	2.3	2.84
FINE-CRUSHED BASALT	1,911.0	1,444.9	2.3	2.84
GLACIOFLUVIAL SAND	1,935.0	1,704.4	1.83	2.75
FINE-CRUSHED ZEOLITE			34.3	1.73

(a) Index properties of candidate clays

Clay Description	Liquid Limit (LL)	Plastic Limit (LP)	Plastic Index (Ip)	Shrinkage Limit (%)	% of soil finer than $-74\mu\text{m}$	% of soil finer than $2\mu\text{m}$	Activity Ip ($\% < 2\mu$)	Specific Gravity (g/cm^3)
Wyoming bentonite	553.1	33.6	519.5	0?	98.03	≤ 98	≥ 5.3	2.77
Oregon bentonite -200 mesh	212.69	38.1	174.6	8.96	99.21	≤ 99	≥ 1.76	2.85
Oregon bentonite 20 to 160 mesh	209.6	41.0	168.58	8.47	98.13	≤ 98	≥ 1.72	2.73
Ringold clay D	63.9	23.1	40.8	19.75	94.58	26	1.57	2.71
Ringold clay C	44.6	25.8	18.8	—	—	—	—	—

(b) Liquid limit versus plasticity index from various clay minerals (from Grim, 1962)

(c) Activity of clay minerals (from Kezdi, 1974)

TYPE OF MINERAL	ACTIVITY Ip/Clay Content
Quartz	0.—
Calcite	0.18
Muscovite	0.23
Kaolinite	0.46
Illite	0.90
Ca-montmorillonite	1.5
Na-montmorillonite	7.5

FIGURE 18
INDEX PROPERTIES OF VARIOUS CLAY MINERALS

activity. The two Oregon bentonites exhibit significantly lower values for these properties. As shown on Figure 18b, Wyoming bentonite has the characteristics of a sodium montmorillonite, while the two Oregon bentonites are similar to a calcium montmorillonite. Results from geochemical testing (Section 4.5.2) also indicate that Oregon bentonite is more calcic than Wyoming bentonite. This distinction is important because the sodium form of montmorillonite exhibits considerably less permeability than the calcium form. Results given by Grim (1962) show that when 50 percent sodium bentonite is present in a quartz sand, the resulting clayey mixture is essentially impervious, while for the same proportions, mixtures made with calcium bentonite have a permeability coefficient of 5×10^{-7} cm/sec.

Although analytical data are not available, Ringold clay D, which has an activity of 1.57 (Plasticity Index divided by clay content), is thought to be primarily composed of smectite clay, which generally exhibits an activity between 1 and 7 (Mitchell, 1976). However, the high percentage of silt present in this soil material and its high shrinkage factor could affect the bond strengths of candidate plug mixtures containing this material.

5.3.7 Evaluation of the Mechanical Properties of Candidate Sand/Clay Mixtures

Compaction, unconfined compression, and swelling tests were carried out on candidate cohesive mixtures for various clay/sand sample ratios using glaciofluvial sand as aggregate and Wyoming bentonite, Oregon bentonite, or Ringold clay D as binding materials. These tests were designed to evaluate the variation in mechanical properties with the amount of clay (versus sand) present in the mixture.

5.3.7.1 Compaction of Candidate Sand/Clay Mixtures

Figure 19 gives the compaction curves for 12 candidate clay mixtures composed of the various clays and glaciofluvial sand, with the proportion of sand ranging from 10 to 70 percent by weight when mixed with the bentonites and from 10 to 50 percent when mixed with Ringold clay. As explained in Section 5.3.3.2, compaction tests were carried out in a 6.35-cm mold. Prior to compaction, clay and sand were thoroughly dry mixed. Water was then thoroughly admixed, and the mixtures were stored for three days in plastic bags to allow hydration of the clay fraction.

Figure 20 shows the relationship between the maximum dry density and clay content of Wyoming, Oregon, and Ringold clay/sand mixtures. For clay contents ranging from 10 to 70 percent (alternatively 10 to 50 percent for Ringold clay D), the curves are linear and decreasing. For equivalent clay contents, mixtures containing Wyoming bentonite were found to be denser than mixtures made with Ringold clay; likewise, mixtures containing Oregon bentonite were denser than those containing Wyoming bentonite. The density difference between each of the three types of mixtures increased with increasing clay content. It is useful to note that even with 50 percent Wyoming bentonite (alternatively 30 percent Oregon bentonite), a soil density representative of competent engineered fills was obtained (greater than or equal to $2,000 \text{ kg/m}^3$). This result suggests that suitable compaction of nearly impervious clayey mixtures is feasible by standard compactive methods. Finally, the -200 mesh Oregon bentonite and the -20/+100 mesh Oregon bentonite were compacted in two separate mixtures with 70 percent glaciofluvial sand in order to study the influence of clay-fraction grain size on compaction. No significant

FIGURE 19
COMPACTION CURVES FOR CANDIDATE SAND/CLAY MIXTURES

EXPLANATION

- Wyoming bentonite
- Oregon bentonite
- △ Ringold clay D

FIGURE 20
THE RELATIONSHIP BETWEEN
MAXIMUM DRY DENSITY AND CLAY CONTENT

difference was observed either in dry density or in optimum water content between the fine and coarse bentonite mixtures.

5.3.7.2 Swelling Pressure of Candidate Bentonite Mixtures

Swelling tests were performed in a consolidometer apparatus on 10 cohesive mixtures in order to estimate the maximum swelling pressure at constant volume for each mixture compacted at the maximum dry density and at the optimum water content, as determined during compaction tests (Section 5.3.3.2). Additional water is made available to the sample during a swelling test through a saturated porous end plate. Curves illustrating the relationship between maximum swelling pressure and percentage of clay in clay/sand mixtures are shown on Figure 21 for the Oregon and Wyoming bentonites.

Figure 21 shows that the Oregon and Wyoming bentonite/sand mixtures have a similar swelling response. The swelling pressure at constant volume is negligible for clay contents less than or equal to 10 percent. For clay contents ranging from 10 to 70 percent, an almost exponential increase of swelling pressure is observed with increasing clay content. For a clay content of 70 percent, swelling pressures as high as 2 MPa were developed. For bentonite content more than or equal to 50 percent, the swelling pressure developed by a confined specimen was such that it was found difficult to constrain it perfectly; a small amount of expansion occurred during the night which had to be corrected the next morning by increasing the loading pressure. As noted by Martin (1975), a small expansion during the test can have a large influence on the measured value of the swelling pressure. Therefore, the measured swelling pressures should be considered as minimum and approximate.

FIGURE 21
SWELLING PRESSURE OF BENTONITE/SAND MIXTURES

Swelling pressure of Ringold clay/sand mixtures was not studied except for a clay content equal to 10 percent where no swelling was observed. However, a lower swelling pressure is expected for Ringold clay (versus bentonites) considering the high silt content of Ringold clay.

5.3.7.3 Rigidity and Cohesion of Candidate Sand/Clay Mixtures

Unconfined compressive tests, including the determination of stress-strain relationships and maximum compressive strengths, were performed on the 10 candidate mixtures compacted at maximum dry density and optimum water content. These tests were designed to evaluate the strength behavior of clay/sand mixtures. In general, high strength and stiffness would be desirable in compacted soil mixtures used in plug designs because the plug material should provide restraint to the surrounding wall rock, which may be under lithostatic and thermomechanical loads. The behavior of this material should be as elastic as possible to maintain the best possible contact with the wall rock.

Figures 22 and 23 present curves showing the variation in unconfined compressive strength and the variation in Young's Modulus with varying clay content. Young's Modulus is taken as the tangent to the stress-strain curve at one percent strain. A notable result was the observed difference in behavior between bentonite/sand mixtures and Ringold clay/sand mixtures. For a clay content of 10 percent, the bentonite mixtures developed strengths 10 times higher and a Young's Modulus eight times greater than Ringold clay/sand mixtures. This result shows the exceptionally high strength of bentonite clays. As expected, mixtures containing Oregon bentonite

FIGURE 22
UNCONFINED COMPRESSIVE STRENGTH OF CLAY/SAND MIXTURES

FIGURE 23
YOUNG'S MODULUS OF CLAY/SAND MIXTURES

developed higher strength and had greater stiffness than those containing Wyoming bentonite. Data published by Grim (1962) indicate that the calcium form of montmorillonite gives the highest strength of all clays when mixed with sand. For clay contents varying from 10 to 50 percent, strength and stiffness increased with increasing clay content. For clay contents varying from 50 to 70 percent, a slight decrease was observed for both parameters with increasing clay content. Maximum values of strength and Young's Modulus were observed for a clay content of 50 percent. Compressive strength and Young's Modulus are exceptionally high, and an unconfined compressive strength of 2.9 MPa with a Young's Modulus of 80 MPa were observed for one Oregon bentonite/sand mixture.

5.3.8 Design and Evaluation of Skip-Graded Aggregate/Clay Mixtures

5.3.8.1 Design of Skip-Graded Aggregate/Clay Mixtures

Skip-graded, coarse-crushed basalt/sand/clay mixtures for potential use in backfill were designed and tested. Materials in these mixtures were composed of -1.9 cm coarse-crushed basalt, glaciofluvial sand, and various clays. A clay/sand ratio of 50 percent was chosen to provide an essentially impervious and self-healing binder. The following three mixtures were tested, and the proportions of the various components are given as weight percents in parentheses:

- Coarse-crushed basalt (68 percent)/Oregon bentonite (16 percent)/glaciofluvial sand (16 percent). In this mixture, the coarse aggregate/sand/clay ratio was selected so that the bentonite/sand mixture filled the void spaces within the aggregate when compacted at its

maximum density. This sample simulated a grain-support framework and was intended to combine relatively low permeability with low compressibility;

- Coarse-crushed basalt (66 percent)/crushed zeolite (17 percent)/Ringold clay (17 percent). In this mixture, crushed zeolite and Ringold clay were substituted for glaciofluvial sand and Oregon bentonite, respectively. The purpose of this substitution was to examine the possibility of using a clay available near the Hanford Site in combination with a material having a high ion exchange potential. This mixture is intended for use in backfill designed to retard radionuclide migration and, at the same time, provide some structural strength; and
- Coarse-crushed basalt (50 percent)/glaciofluvial sand (25 percent)/Wyoming bentonite (25 percent). In this mixture, the coarse aggregate/sand/clay ratio was designed with a high percentage of clay in order to simulate a matrix support fabric (with clay as the matrix). This mixture is primarily designed to be an almost impervious backfill that has substantial self-healing potential.

5.3.8.2 Evaluation of the Mechanical Properties of Skip-Graded Aggregate/Clay Mixtures

No swelling tests were attempted on these candidate mixtures; special test equipment would be necessary for the maximum aggregate sizes considered in these tests. Results on compaction and unconfined compression tests are given in Figure 24.

(a) Compaction curves for skip-graded aggregate/clay

EXPLANATION

Mixture (A):
 50% Coarse-crushed basalt
 25% Glaciofluvial sand
 25% Wyoming bentonite

Mixture (B):
 68% Coarse-crushed basalt
 16% Glaciofluvial sand
 16% Oregon bentonite

Mixture (C):
 66% Coarse-crushed basalt
 17% Crushed zeolite
 17% Ringold clay D

(b) Unconfined compressive strength curves for skip-graded aggregate/clay

FIGURE 24

MECHANICAL BEHAVIOR OF SKIP-GRADED AGGREGATE/CLAY MIXTURES

The most effective compaction and maximum unconfined compressive strength results were obtained for the Wyoming bentonite/glaciofluvial sand/coarse-crushed basalt mixture. A maximum dry density of 2,266 kg/m³ (at an optimum water content of 9.3 percent) and an unconfined compressive strength of 1.45 MPa were measured for this sample. A somewhat lower maximum dry density (2,195 kg/m³) and an unconfined compressive strength half that of the first mixture were measured for the mixture of Oregon bentonite, glaciofluvial sand, and coarse-crushed basalt. As expected, an even lower density was obtained for the Ringold clay/zeolite/coarse-crushed basalt mixture (2,066 kg/m³) due principally to the high porosity and low specific gravity of the crushed zeolite. However, this density still has a range judged representative of multiple-purpose engineered fills. Moreover, the unconfined compressive strength developed by this last mixture was appreciable.

5.3.9 Results of Screening Test on Compacted Earth Materials

Geological reconnaissance and various index and mechanical tests resulted in the selection of Ringold clay D as a preferred clay from among several fine-grained sedimentary units in the Pasco Basin. Although Ringold clay is considered the best performing clayey soil when compared to other clay units available near the Hanford Site, this clay did not exhibit the optimum characteristics for use in plugs when compared to clays available from more distant sources. Ringold material has a high shrinkage limit, high silt content, and relatively low compaction.

A comparison of clay activity values showed that Wyoming bentonite has characteristics close to a sodium montmorillonite, and Oregon bentonite has characteristics close

to a calcium montmorillonite. Consequently, Wyoming bentonite mixtures are expected to have higher compressibility, lower shear strength, and lower permeability.

Index tests performed on candidate non-cohesive granular materials indicated that glaciofluvial sand and crushed basalt are the most desirable aggregates for use in skip-graded aggregate/clay mixtures. Both offer acceptable grain-size distribution and structural strength. In contrast, crushed zeolite appears to be a very weak aggregate, but would be acceptable for use in backfill where an increase in ion exchange potential and sorption capacity are considered desirable.

Relatively good densities were achieved by impact compaction of bentonite/sand mixtures for clay contents lower than or equal to 50 percent in the case of Wyoming bentonite and 30 percent in the case of Oregon bentonite. Unconfined compressive strength on clay/sand samples indicated that bentonite/sand mixtures had considerably higher strength than Ringold clay/sand mixtures.

Swelling pressures at constant volume were measured for bentonite/sand mixtures compacted to maximum density at various optimum water contents and tested in a consolidometer under immersed water conditions. Swelling pressures were negligible for samples with clay contents of 10 percent, but increased exponentially to values reaching 2 MPa when the clay content increased to 70 percent. If damaged by hydraulic fracturing or mechanical shearing, the swelling pressure behavior may provide compacted plug materials with cohesive self-healing properties.

Results of compaction and compression tests on skip-graded aggregate/clay mixtures show the best density and strength for mixtures containing 25 percent Wyoming bentonite, 25 percent glaciofluvial sand, and 50 percent -1.9 cm coarse-crushed basalt. Density and strength in the range of multiple-purpose engineered fills and appreciable strength were obtained for mixtures composed of Ringold clay, crushed zeolite, and crushed basalt, although the values for these properties were comparatively lower than all other candidate, skip-graded aggregate/clay mixtures.

5.4 CLAY SLURRIES - SCREENING TESTS

5.4.1 Candidate Materials

Candidate materials that were mixed with water to form clay slurries and the source for each material are listed in Table XVIII. A description of the test slurries and proportions of components in these slurries are given in Table XIX. The content of solid clay particles in slurries varied from 2 percent up to as much as 17 percent by weight.

5.4.2 Testing Program and Procedures

Preliminary screening tests of clay slurries included:

- Determination of the densities of fresh slurries using a container of known weight and volume;
- Determination of the flow properties of slurries by measuring the time of discharge of a specified volume of slurry from a standardized flow cone; and

TABLE XVIII

MATERIALS USED IN SCREENING TESTS ON
CLAY SLURRIES

<u>Material</u>	<u>Source</u>
Shurgel (processed bentonite)	Baroid National Brand
Aquagel (processed bentonite)	Baroid National Brand
Wyoming bentonite	Baroid National Brand
Ringold clay from Unit D	Pasco Basin

TABLE XIX
QUALITATIVE RESULTS OF THIXOTROPY TESTS ON CLAY SLURRIES

SLURRY DESIGN		AS MIXED	1 DAY	3 DAYS	7 DAYS
A - 3 SHURGEL	2% Solids	Low viscosity liquid	Low viscosity liquid	Low viscosity liquid	Low viscosity liquid
	4% Solids	Low viscosity liquid	Low viscosity liquid	Moderate viscosity liquid	Moderate to high viscosity liquid
	6% Solids	Low viscosity liquid	Moderate to high viscosity liquid	Some shear strength apparent by indentation left in surface of sample	Increased shear strength indicated by deeper indentation left in surface of sample
	8% Solids	Very high viscosity liquid	Some shear strength apparent by indentation left in surface of sample	Increased shear strength indicated by deeper indentation left in surface of sample	Greater shear strength indicated by hole left in surface of sample
A - 4 WYOMING BENTONITE	2% Solids	Low viscosity liquid	Low viscosity liquid		Cloudy water, solids at bottom of container
	4% Solids	Low viscosity liquid	Low viscosity liquid		Low to moderate viscosity liquid, some settling of solids
	6% Solids	Low viscosity liquid	?		Moderate to high viscosity liquid
	8% Solids	Low viscosity liquid	Moderate viscosity liquid		High viscosity liquid
A - 5 AQUAGEL	2% Solids	Low viscosity liquid	Low viscosity liquid		Cloudy water, solids at bottom of container
	4% Solids	Low viscosity liquid	Low viscosity liquid		?
	6% Solids	Low viscosity liquid	?		Moderate to high viscosity liquid
	8% Solids	Low viscosity liquid	Moderate to high viscosity liquid		Some shear strength apparent by indentation left in surface of sample
A 77 W/A 3 RINGOLD CLAY 98% W/SHURGEL 2%	2% Solids	Essentially cloudy water	Clear water, solids at bottom of container		Clear water, solids at bottom of container
	4% Solids	Essentially cloudy water	Cloudy water		Clear water, solids at bottom of container
	6% Solids	Essentially cloudy water	Cloudy water		Clear water, solids at bottom of container
	8% Solids	Essentially cloudy water	Cloudy water		Clear water, solids at bottom of container

- Evaluation of the thixotropic properties of slurries by measuring the shear strength of the slurry at increasing time using a laboratory vane shear test.

Parameters of gel strength, thixotropy (increase of gel strength with time), and stability (ability of the solids to remain in suspension) define the principal properties needed by slurry mixtures to perform the anticipated design functions for a borehole plug. Screening tests were designed to identify the best mixtures of candidate materials in a slurry to obtain the best values of the parameters.

5.4.3 Preliminary Test Results and Discussion

Tests were conducted to evaluate the density, flow properties, and thixotropic properties of candidate slurries having solids content varying from 2 to 17 percent by weight. The results of these tests are presented in Figures 25 and 26 and Table XIX.

5.4.3.1 Slurry Densities

For complete dispersion of solids, a linear relationship can be demonstrated between slurry density and solids content, as shown in Figure 25. The slope of this straight line, as drawn through a plot of experimental data points, is a function of the specific gravity of the solids. Note that the point corresponding to a slurry containing 15 percent Aquagel was plotted at a density lower than was expected because of the presence of several air voids in the sample used for the density determination. For the slurry in which solids consisted of 98 percent Ringold clay and 2 percent Wyoming bentonite, there was a great deal of scatter in the test results due to the difficulty in obtaining a representative

EXPLANATION

- X Water alone
- Shurgel (A-3)
- Aquagel (A-5)
- △ Wyoming bentonite (A-4)
- 98% Ringold clay (A-77)
2% Wyoming bentonite (A-4)
- (e.s.) Excess silt
- (a.v.) Air void

FIGURE 25
DENSITIES OF CLAY SLURRIES

FIGURE 26
FLOW TIME OF CLAY SLURRIES

sample for density determination. This difficulty was primarily caused by the high silt content of Ringold clay D; the solids rapidly settled whenever agitation of the slurry ceased, thereby effectively reducing the solids content of the slurry. Thus, it was difficult to produce a consistent slurry when using Ringold clay. With the exception of these discrepancies, the test results do show the linear relationship between slurry density and solids content. The slurries consisting of Shurgel and Aquagel produced the greatest densities.

5.4.3.2 Flow Properties of Slurries

In conjunction with tests to determine slurry densities, the same slurry mixtures were used to determine the flow properties (viscosity) of slurries at various solids content by measuring the time required for a given volume of slurry to flow out of a test funnel. It should be noted that the flow time of water at 25°C was approximately 8.3 seconds. Tests performed to monitor consistency indicated that test repeatability was reasonable (about ± 0.20 second).

As shown in Figure 26, for slurries with solids consisting of Shurgel, Aquagel, or Wyoming bentonite, the viscosity is close to that of water for solids content less than 6 percent. The viscosity increased rapidly for solids content above 6 percent. For solids content greater than 9 percent (the consistency of a heavy drilling mud), the slurries became too viscous to flow through the cone used for this test. The slurry containing Shurgel increased in viscosity (with increase in solids content) much more rapidly than slurries containing either Aquagel or Wyoming bentonite, both of which increased equally in viscosity with increasing solids content. However,

the slurry that contained 98 percent Ringold clay and 2 percent Wyoming bentonite maintained a viscosity close to that of water for all solids content tested, including solids content as high as 17 percent. This result confirms the instability of this mixture as a permanent suspension in a slurry because of the rapid settling of solids upon cessation of mixing.

5.4.3.3 Thixotropic Properties of Slurries

After evaluating the results of tests for slurry densities and flow properties, it was possible to select slurry mixtures that received further testing with respect to thixotropic (shear strength) properties. In an attempt to quantify test results, laboratory vane shear tests were performed. However, the test apparatus was not sensitive enough to measure the low shear strength associated with the slurries, and qualitative descriptions given in Table XIX must be used to present the results of these tests. Each time a vane shear test was performed on a slurry sample, the sample condition was monitored by taking a solids content specimen from the sample (Figures 27 and 28). These specimens were taken by scraping some slurry from the top of the sample with a spoon. It was this procedure that produced indentations and holes in the surface of samples, as noted in Table XIX. These indentations and holes are considered a valid basis for an initial qualitative comparison of shear strength because the slope stability of the cut of any material is a function of its shear strength.

The descriptions given in Table XIX are presented to illustrate the following test results: (1) for solid contents less than 6 percent, no apparent shear strength was developed by any of the slurries tested; (2) 7 days after being mixed, apparent

FIGURE 27

VARIATION OF SOLIDS CONTENTS (2% and 4%) OF CLAY SLURRIES

FIGURE 28

VARIATION OF SOLIDS CONTENTS (6% and 8%) OF CLAY SLURRIES

shear strength was only developed by slurries containing 6 percent and 8 percent Shurgel and 8 percent Aquagel; (3) the slurry containing 6 percent Shurgel developed apparent shear strength after a period of 3 days, while the slurry containing 8 percent Shurgel developed apparent shear strength after a period of only 24 hours; and (4) the slurry containing 8 percent Shurgel developed sufficient shear strength after a period of 7 days to maintain vertical sides of a groove in the sample. However, this shear strength was still too small to be measured with the laboratory vane shear apparatus (the minimum measurable shear strength is 1.4 g/cm^2). These results indicate that, in terms of shear strength, slurries should contain at least 6 percent by weight of solids and that the greatest strength will be developed by slurries containing Shurgel.

These results were further substantiated by data obtained by continuous monitoring of thixotropy tests (Figures 27 and 28). The change in solids content for a sample, as shown in these figures, is given as the percent change from the original solids content of that sample; that is, -10 percent indicates that at the surface of the sample, there were 10 percent fewer solids than when the sample was originally prepared. These figures illustrate the extent to which the solids in a slurry remained "suspended" throughout the slurry or "settled" towards the bottom of the sample. The results indicate that Shurgel solids essentially remained suspended throughout the sample for all solids content tested, whereas in the mixture of 98 percent Ringold Clay with 2 percent Shurgel, solids settled to the bottom of the sample for all solids content tested (Table XIX). The slurries containing Aquagel and Wyoming bentonite exhibited significant settling of solids for mixtures containing 2 percent solids; however, for solids

content of 6 percent and 8 percent, the solids essentially remained suspended throughout the sample.

If this phenomenon of "suspended" and "settling" solids can be explained in terms of the repulsion and attraction of individual clay particles, these results appear to be consistent with those shown in Table XIX. That is, development of viscosity and shear strength in a stable slurry is consistent with the ability of the clay particles to remain suspended throughout the slurry volume. Similarly, these results are considered consistent with results shown in Figures 25 and 26 in which increases in slurry density and viscosity were related to the ability of clay particles to remain suspended throughout the slurry volume.

5.4.4 Results of Screening Tests on Clay Slurries

Screening tests on four candidate clays used in slurries demonstrated:

- The development of gel strength for slurries composed of more than 6 percent Shurgel, Aquagel, or Wyoming bentonite;
- A high increase in viscosity of Shurgel, Aquagel, or Wyoming bentonite slurries for solids content more than 8 percent;
- A segregation of particle sizes and absence of gel formation in slurries composed of Ringold clay plus Wyoming bentonite; and
- The best gel strength, thixotropy (increase of gel

strength with time), and stability (ability of the solids to remain in suspension) were observed for slurries mixed with Shurgel (processed bentonite). A mixture of 7 percent by weight of dry Shurgel in water is recommended to obtain the best shear strength with good stability.

5.5 CEMENTITIOUS GROUTS AND CONCRETES - PERFORMANCE TESTS

5.5.1 Materials

The screening test results for cementitious mixtures (presented in Section 5.2) led to the selection of materials for more detailed performance test evaluations: (1) on the basis of workability, volume change, and structural strength for mixtures to be placed at locations where temperatures are expected to be low (less than 100°C); and (2) on the basis of workability, volume change, structural strength, and thermal stability for mixtures to be placed at locations where high temperatures are expected (greater than 100°C). A list of materials employed in performance tests is given in Table XX.

5.5.2 Mixture Designs

5.5.2.1 Grout Mixtures

The proportions of components used in grout samples were chosen to produce relatively dense, impervious but easily pumpable mixtures. Mixture guidelines were as follows:

- Water/cement ratios were selected to produce a flow of 16 ± 1 seconds as determined with the C-79-77 "Test Method for Flow of Grout Mixtures (Flow Cone Method)" (U.S. Army Corps of Engineers, 1978);

TABLE XX
MATERIALS USED IN PERFORMANCE TESTS
FOR CEMENTITIOUS MIXTURES

Cementitious Materials

Portland Type V cement and silica flour (high temperature locations: $T \geq 100^{\circ}\text{C}$)

Portland Type V cement and Lassenite (moderate temperature locations: $T < 100^{\circ}\text{C}$)

TXI Chem Com cement and Lassenite (low temperature locations: $T \leq 50^{\circ}\text{C}$)

Fine Aggregates

Glaciofluvial sand or crushed basalt sand (from the Hanford Site)

Coarse Aggregates

Minus 2.5 cm crushed river gravel or crushed basalt gravel (from the Hanford Site)

Additives

Water-reducing retarder agent (Plastiment)
-325 mesh polished, leafing-type aluminium powder

- Cement/pozzolan/sand proportions expressed by weight were 5 parts cement to 2 parts pozzolan and 6 parts sand;
- The aluminum powder to cement ratio equaled 0.03 percent by weight (only in portland cement mixtures); and
- The addition of 90 ml of Plastiment were used per bag of cement (42.6 kg).

5.5.2.2 Concrete Mixtures

Mixtures were designed following U.S. Bureau of Reclamation recommended procedures for concretes containing a WRA, fine aggregate, 2.5-cm maximum size coarse aggregate, and a slump of 7.5 to 10 cm at the mixer. Corresponding proportions were then adjusted to ascertain actual values of the fineness modulus of sand. Data giving the relative proportion of pozzolan and silica flour used in cements are the same as those presented in Section 5.2.2 for cement mortars:

- A pozzolan to cement ratio of 20 percent; and
- A silica to silica plus cement ratio equal to 35 percent.

5.5.3 Testing Program and Procedures

Performance tests of candidate grout and concrete mixtures included: (1) standard index tests of freshly prepared cementitious mixtures; (2) density, porosity, volume change, and strength determinations of hardened mixtures; and (3) model

testing, including the determination of the permeability and bond strength of cementitious mixtures and basalt host rock. A list of testing methods is presented in Table XXI. Special test methods (including model testing of concrete materials and basalt host rock) are described in the following sections.

5.5.3.1 Sampling and Curing of a Plug/Basalt (Host Rock) Model

Two types of plug/basalt models were prepared: one using a clean basalt surface, and the other using a mud-contaminated basalt surface:

- The preparation of a clean basalt rock sample was intended to simulate placement of a grout plug (concrete plug) against the clean wall of a borehole (borehole, shaft, or tunnel). Freshly mixed grout (concrete) was placed in a 2.60-cm (6.45-cm for concrete tests) diameter hole drilled down the center of a piece of basalt core which was 5.08 cm in diameter (10.16 cm for concrete tests) and 4.45 cm long (7.62 cm for concrete). After 24 hours of curing in a moist room and 6 days of curing in a lime-water bath at standard temperature, the plug/basalt models were autoclaved under the steam pressure of water at 100°C for 72 hours. Plug/basalt models were then removed from the autoclave and again placed in the lime-water bath until testing.
- Mud is the common drilling fluid used in boreholes. It is circulated down to the drill bit, then back out of the hole in order to remove cuttings, cool the bit, and lubricate the drill stem. The drilling mud

TABLE XXI
PERFORMANCE TEST PROCEDURES USED
FOR CEMENTITIOUS MIXTURES

<u>Grout Test Methods</u>	
CRD-C 79-77 ^a	Test method for flow of grout mixtures
ASTM C-191 ^b	Setting time by vicat needle
CRD-C 81-74 ^a	Test method for expansion of grout mixtures
API RP-40 ^c	Dry density determination by caliper method
API RP-40 ^c	Porosity determination by buoyancy method
CRD-C 588-78A ^a	Restrained volume change of hardened cement grouts
Modified ASTM C-39 ^d	Unconfined compressive strength of cylindrical cement specimens. The modification specifies the use of a 5-cm diameter per 10-cm height grout cylinders
Special Test Method	Bond strength of cement grout/basalt (host rock) at ambient temperature
Special Test Method	Bond strength of cement grout/basalt (host rock) at high temperature
Special Test Method	Bond strength of cement grout/basalt (host rock) at ambient temperature with previous mud contamination of the basalt (host rock) walls
Special Test Method	Permeability of cement grout/basalt (host rock) at ambient temperature

(continued)

TABLE XXI (continued)

<u>Concrete Test Method</u>	
ASTM C-143 ^d	Slump test of freshly mixed concrete
ASTM C-231 ^d	Air content of freshly mixed concrete by the pressure method
ASTM C-138 ^d	Unit weight of freshly mixed concrete
ASTM C-157 ^d	Length change of hardened cement concrete (drying shrinkage)
ASTM C-29 ^d	Unconfined compressive strength of cylindrical concrete specimens
Special Test Method (see Text)	Permeability of concrete/basalt (host rock) at ambient temperature
^a U.S. Army Corps of Engineers (1978) ^b ASTM (1973) ^c American Petroleum Institute (1960) ^d ASTM (1977b)	

produces a cake which builds up on the borehole wall. Consequently, a mud cake can be present prior to plugging the borehole. Mud contamination of a borehole was simulated by filling a hole drilled lengthwise into a basalt (host rock) core with bentonite slurry (8 percent by weight of Shurgel) prior to plugging. The bentonite slurry was then left set for at least two hours inside the basalt core. The mud slurry was drained from the bottom of the piece of core before simulated plugging with concrete, as described above.

5.5.3.2 Bond Strength of a Cement Plug/Basalt (Host Rock) Model at Ambient Temperature

Bond strength in the cement plug/basalt model was obtained by axially loading the miniature plug until failure of the plug/wall rock bond occurred. Plug loading was accomplished using a mechanical loading frame to push a piston (2.54 cm in diameter) which was concentrically aligned with the 2.60-cm diameter plug. To allow plug extrusion, a flat metal loading base, which had a 3.18-cm diameter hole drilled through it, was placed at the bottom of the basalt when testing grout plugs. Bond strength values were mathematically obtained by dividing the maximum loading force obtained during plug extrusion by the contact area between the plug and the wall rock.

5.5.3.3 Bond Strength of a Cement Plug/Basalt (Host Rock) Model At High Temperature

Bond strengths of the miniature plug models were also determined using the maximum assumed temperature of 100°C at plug seats (see Table A-I, Appendix A) resulting from thermal

loading of radioactive wastes stored in the repository. Prior to testing, the plug/basalt model was dried for 48 hours at 100°C in a conventional laboratory oven. The model was then removed from this oven and immediately placed in the preheated chamber of a special split test oven maintained at a constant temperature of 100°C. Thermocouples directly connected to an electronic temperature readout monitored the oven chamber temperature throughout the duration of the test runs. Temperatures in the plug were checked prior to testing by the readout of a thermocouple inserted inside the plug. The test oven was set up between the loading plates of a 45,000-kg hydraulic press. This configuration, which was designed to minimize the temperature gradient inside the oven chamber, included: (1) a permanent, insulated 15-cm diameter pedestal (protruding from the lower loading plate of the hydraulic press and extending up into the oven); and (2) a 10-cm diameter insulated loading ram (protruding through the top of the oven to the pressure cell directly connected to the upper loading plate of the hydraulic press). Plug extrusion and bond strength calculations followed the same procedures as for low temperature bond strength determination.

5.5.3.4 Permeability of a Cement Plug/Basalt (Host Rock) Model at Ambient Temperature

Permeability tests of cement plug/basalt (host rock) models were carried out inside a conventional triaxial cell using the falling head method. A pressure differential of 0.05 MPa for concrete plugs and 0.03 MPa for grout plugs was applied between the top and the bottom of the full surface of the composite samples, corresponding to an approximate value of 70 for the hydraulic gradient. Thus, the permeability measurement represents an average permeability for the entire plug/basalt model.

5.5.4 Test Results and Discussion

Test results are given for each cementitious mixture on Figures 29 to 34.

5.5.4.1 Grout Performance

- The initial setting time for the three grout mixtures was greater than 6 hours. The time of set could be reduced by decreasing the amount of the WRA (Plastiment) in the mixtures. However, a final evaluation of the setting time should be done under in-situ downhole temperature conditions because an increase in temperature may decrease the setting time;
- Oven dry densities of grout composed of Chem Com TXI cement plus Lassenite (G-TXI-L) and grout composed of portland cement Type V plus Lassenite (G-V-L) were found to be the same (1.64 g/cm^3), while a significant difference in porosity was observed (42.3 percent for G-TXI-L and 33 percent for G-V-L). Data on water cement ratios indicated that porosity data were consistent. Thus, oven-dry densities may be misleading. An explanation may be the difference in specific gravity between Chem Com TXI and portland cement Type V. The high value of oven-dry density for the grout composed of portland cement Type V plus silica flour (G-V-S) is due to the high specific gravity of the silica flour (2.65 g/cm^3) when compared with the specific gravity of Lassenite (2.43 g/cm^3).

FIGURE 29
SUMMARY OF GROUT PERFORMANCE:
FOR HIGH TEMPERATURE LOCATION ($T \geq 100^\circ\text{C}$)

FIGURE 30

**SUMMARY OF GROUT PERFORMANCE:
FOR MODERATE TEMPERATURE LOCATION (T < 100°C)**

FIGURE 31

**SUMMARY OF GROUT PERFORMANCE:
EXPANSIVE GROUT FOR RELATIVELY LOW TEMPERATURE LOCATIONS ($T \leq 50^\circ\text{C}$)**

FIGURE 32
SUMMARY OF CONCRETE PERFORMANCE:
FOR HIGH TEMPERATURE LOCATION ($T \geq 100^\circ\text{C}$)

FIGURE 33

**SUMMARY OF CONCRETE PERFORMANCE:
FOR MODERATE TEMPERATURE LOCATION (T < 100°C)**

FIGURE 34

**SUMMARY OF CONCRETE PERFORMANCE:
FOR RELATIVELY LOW TEMPERATURE LOCATIONS (T ≤ 50°C)**

- The restrained volume change of G-TXI-L grout did not meet the non-shrink grout requirements specified in the Corps of Engineers "Handbook for Concrete and Cement" C-588 (U.S. Army Corps of Engineers, 1978) because a slight shrinkage (0.05 percent) was observed after 28 days of wet curing. This shrinkage cannot be explained by the addition of Lassenite because the presence of a pozzolan in a cement mixture generally decreases shrinkage. Further testing is needed to refute or confirm this result. The 28-day restrained shrinkage result for G-V-L was found to be twice that for the G-TXI-L. Nonetheless, it is considerably lower than that reported earlier for portland cement Type V mortar without an additive, even though a higher water/cement ratio was used. A non-shrink grout could be obtained by adding a slightly greater amount of aluminum powder and/or Plastiment and/or Lassenite in the G-V-L mix. No shrinkage was observed for G-V-S grout, indicating that the addition of finely ground aluminum powder tends to reduce the shrinkage behavior of cement mixtures.
- The "28-day" compressive strength measurements of grout cylinders under standard curing and testing temperatures were found to be 39.2 MPa for G-TXI-L, 28.6 MPa for G-V-L, and 24.8 MPa for G-V-S. These values are within the design range needed for plugs to restrain the expected lithostatic and thermomechanical loading forces at plug-seat depths (see Table A-I, Appendix A).
- Grout plug/basalt (host rock) bond strengths measured at standard temperature are significantly higher for G-TXI-L (10.8 MPa) and G-V-L (10.0 MPa) than for G-V-S (4.3 MPa). The high values and the similarity in bond

strengths for G-V-L and G-TXI-L are attractive for better meeting plug/wall rock interface performance requirements and tend to confirm the mixture design studies conducted during screening tests.

- Significantly lower bond strengths were obtained for models with mud-contaminated drill hole walls, which suggests that in actual practice, boreholes should be flushed before plugging.
- Comparisons of bond strengths obtained at standard temperature with bond strengths obtained at high temperature (100°C) indicate a decrease in bond strength with increasing temperature. Percentage deterioration of bond strength is 19 percent for G-V-S, 61 percent for G-V-L, and 88 percent for G-TXI-L. Once again, the addition of silica flour greatly improved the high temperature performance of the cement mixtures. Note that these bond strengths take into account shrinkage of grout plugs caused by 48-hour oven curing prior to testing.

The test data show model plugs composed of portland cement Type V have a permeability of less than 10^{-8} cm/sec, which is surprisingly low considering the relatively high porosity of these mixtures. The model plug composed of Chem Com TXI cement is somewhat more permeable (3.5×10^{-8} cm/sec). It should be remembered that each model plug was subjected to a 72-hour curing period in an autoclave at 100°C prior to testing. This procedure was chosen to accelerate the curing of the grout mixtures in order to meet project time constraints. As mentioned earlier, cement mixtures containing Chem Com TXI cement exhibited a deterioration in structural strength when

cured at elevated temperature. Consequently, lower permeability may be expected for mixtures cured at ambient temperature.

5.5.4.2 Concrete Performance

- The mixture containing C-V-S had a slightly higher slump (11.43 cm) than the other concrete mixtures. This should be considered when comparing performance results of the various concrete mixtures. Thus, for a lower slump, C-V-S may have a higher density and strength and lower permeability.
- Once again, concrete mixtures containing C-TXI-L had a higher porosity. Porosity and density data for the three concrete mixtures seemed consistent and were characteristic of relatively dense concretes.
- As in the case of the grout, the concrete mixture containing Chem Com TXI cement does not exhibit the expected expansive behavior but shows a slight shrinkage (0.03 percent) after the standard 28-day dry curing. In fact, no significant difference in volume change was observed between the three concrete mixtures. As in the case of the grout, C-V-S exhibited the lowest shrinkage, while the concrete mixture containing C-V-L had the highest.
- The "28-day" compressive strength measurements for concrete cylinders were 42.1 MPa for C-V-S, 37.9 MPa for C-TXI-L, and 36.5 MPa for C-V-L. Concretes containing silica flour appear to have the greatest structural strength, even when cured under standard temperatures.

- The results of permeability tests on concrete plug/basalt (host rock) models confirm the results obtained on model grout plugs. C-TXI-L is slightly more permeable (9.26×10^{-9} cm/sec) than C-V-L (3.7×10^{-9} cm/sec) and C-V-S (1.5×10^{-9} cm/sec). The permeability obtained for C-V-S is on the order of the permeability of the basalt core container (assumed to be 10^{-9} cm/sec from Table A-I, Appendix A). This result suggests that the design of a concrete plug having similar hydraulic characteristics as those reported for basalt flows at the Hanford Site is possible (see Table A-I, Appendix A).

5.6 COMPACTED EARTH MATERIAL - PERFORMANCE TESTS

5.6.1 Materials and Mixtures

Except for the elimination of six fine-grained sediments from the Pasco Basin, no further screening was attempted in the first phase of physical testing described in Section 5.3. Some of the materials and mixtures that survived the screening tests may be more or less suitable than others as potential plug components. However, no definitive arguments were found to justify not testing those mixtures remaining after the screening tests on compacted earth materials. Therefore, mixtures considered in this section are the same as those described in Section 5.3.2, except for the deletion of the six materials from the Pasco Basin.

5.6.2 Testing Program and Procedures

Performance tests included: (1) model tests of the bond strength and permeability of miniature compacted soil plugs; and (2) consolidation tests on compacted sandy clay mixtures. Consolidation tests were made using ASTM D-2435 method "One Dimensional Consolidation of Soil Materials" (ASTM, 1978b). Bond strength tests were carried out using the same procedures as for bond strength determinations on concrete plug/basalt (host rock) models described in Section 5.5.3. Plug placement simulation and permeability tests are described below.

5.6.2.1 Compacted Soil Plug Model Preparation

Prior to compaction, soil components of the model plug were dry-mixed. Subsequently, sufficient water was added to dampen the mixture to optimum water content. This mixture was then stored in sealed plastic bags and allowed to hydrate for two days. The geometric characteristics of the basalt (host rock) core used to model bond strengths during test runs (and alternatively, to model permeability tests) were chosen as follows: the outer core diameter was 10.16 cm, the internal hole diameter (drilled lengthwise into the core) was 6.35 cm, and the core length was 13.97 cm (and alternatively for permeability tests, 7.62 cm). Borehole walls were thoroughly washed and allowed to air-dry before placement and compaction of the simulated plug materials. Samples simulating mud contamination of boreholes were prepared using the same procedure described in Section 5.5.3.1. Soil placement was performed by compacting the soil materials in the 6.35-cm diameter hole drilled into the basalt core in five equal layers (three layers for permeability tests); this placement would give a total length of compacted soil not exceeding 12.5 cm

(7.62 cm for permeability tests), such that 95 percent of maximum dry density was achieved using the compacting method described earlier in Section 5.3.3.2.

5.6.2.2 Permeability Measurements of Compacted Soil Plug/Basalt (Host Rock) Models

Special permeameters and cap plates were designed for the permeability testing of the miniature soil plugs which have 15.24-cm diameter bases. The cap plate has a recessed 7.62-cm diameter O ring and a 6.35-cm diameter porous stone through which channels (3 mm in diameter) are drilled and machined such that a flow path exists between the porous stones and hydraulic fittings screwed into the plate. Base plate and cap plate were placed directly on the dressed surface of the basalt (host rock) core containing the compacted soil materials. As in the case of cement plugs, permeability was determined using the falling head method. However, to avoid any potential for particle migration, only a 0.003 MPa pressure differential was applied between the top and the bottom of the compacted plug, corresponding to an approximate hydraulic gradient of 4.

5.6.3 Test Results and Discussion

5.6.3.1 Bond Strength of Compacted Soil Plug

Results of bond strength tests carried out at ambient temperature on soil plugs compacted in clean basalt (host rock) cores are given on Figure 35 for Wyoming bentonite, Oregon bentonite, and Ringold clay D, each mixed with glaciofluvial sand. Clay content ranged from 10 to 70 percent. Highest bond strengths were observed for Oregon bentonite/sand mixtures for all clay contents, closely followed by bond strengths obtained

EXPLANATION

- Wyoming bentonite
- Oregon bentonite
- △ Ringold clay

FIGURE 35
BOND STRENGTH OF CLAY/SAND MIXTURES AT AMBIENT TEMPERATURE

for Wyoming bentonite/sand mixtures. Ringold clay D/sand mixtures had significantly lower bond strengths, particularly for clay content less than 50 percent. The shapes of curves plotted on the basis of experimental values for bond strength are similar for all three types of clay.

Maximum bond strength was observed for a clay content equal to 10 percent. For clay contents varying between 10 and 30 percent, bond strengths decreased sharply. Subsequently, bond strengths alternately increased and decreased for clay content ranging from 30 to 50 percent and from 50 to 70 percent.

The variation in curve shapes for clay content varying from 10 to 50 percent indicate a change in the physical nature of the bond between the compacted soil plug and the basalt (host rock). This change is interpreted as a transition from an essentially frictional to an essentially cohesive bond. This hypothesis is supported by comparing (for increasing clay percentage) the variation of the unconfined compressive strength of clay/sand mixtures, which is considered to be an approximation of twice the cohesion of the clay mixtures (Figure 36), and the variation in the friction angle. In the absence of specific data for the friction angle, Figure 36 gives the variation of the residual friction angle (expressed by its tangent) with variations in the clay content, as obtained by Kenney (1967) for sodium montmorillonite/quartz sand mixtures under an effective confining pressure of 0.1 MPa.

Figure 36 indicates a low and approximately constant value of the friction angle for clay content greater than 20 percent. Accordingly, variations in bond strength should follow these values of cohesion (unconfined compressive strength). Thus, the bond between the compacted soil plug and basalt host rock

EXPLANATION

- (A) ○ Wyoming bentonite compressive strength values obtained in WCC physical testing
- (B) ● Tangent ϕ residual of sodium montmorillonite/quartz sand mixtures under $\sigma'_n = 0.1$ MPa (Kenney, 1967)

FIGURE 36
COMPARISON OF THE FRICTIONAL AND COHESIVE BEHAVIOR
OF BENTONITE/SAND MIXTURES

is essentially cohesive in nature. For clay content ranging from 10 to 20 percent, the linear increase in cohesion is accompanied by a sharp decrease in friction angle, and the nature of the bond varies from frictional to cohesive. Accordingly, the minimum value for bond strength is expected to occur for clay content between 10 and 20 percent. Further testing is needed to precisely locate this minimum.

This hypothesis of a transition in bond nature from frictional to cohesive seems to be in agreement with the shapes of curves giving the change in bond strength with the percent of sliding deformation. Typical curves given in Figure 37 for 10 percent clay content ratios of Wyoming bentonite and sand show a relatively slow differential increase in bond strength until the peak value is reached, which is followed by a slow decrease in strength (residual bond strength). These curves also show a greater differential increase in bond strength followed by a sharp loss of cohesion for clay content greater than 10 percent. Note that for all clay percentages, significant residual bond strength was observed after the peak bond strength was achieved, indicating only a partial destruction of the bond under large sliding deformations. Other data (not included in this report) indicate that the bond strength is strongly dependent on percent compaction. Bond strengths of Oregon bentonite/sand mixtures (for a clay content of 10 percent) exhibited a 70 percent decrease when soil plugs compacted at 95 percent and at 87 percent were compared.

Table XXII summarizes the results of bond strength measurements for: (1) soil plugs compacted at ambient temperature in a mud-contaminated basalt (host rock) core; and (2) soil plugs compacted at high temperature (100°C) in a clean basalt (host rock) core for two different clay contents of 10 and 50 percent:

FIGURE 37

**BOND STRENGTH -SLIDING STRAIN CURVES FOR SAND/CLAY MIXTURES,
CONTAINING WYOMING BENTONITE AND GLACIOFLUVIAL SAND**

TABLE XXII
SUMMARY OF BOND STRENGTH DATA
FOR SELECTED CLAY/SAND MIXTURES

MIXTURE COMPONENTS	BOND STRENGTH @ AMBIENT TEMPERATURE (MPa)	BOND STRENGTH @ AMBIENT TEMPERATURE ON MUD CONTAMINATED HOST ROCK (MPa)	BOND STRENGTH @100°C (MPa)
10% Wyoming bentonite 90% Glaciofluvial sand	0.11	0.67	≈7*
50% Wyoming bentonite 50% Glaciofluvial sand	0.80	0.30	0.51
10% Oregon bentonite 90% Glaciofluvial sand	0.11	0.10	≈7*
50% Oregon bentonite 50% Glaciofluvial sand	0.94	0.45	0.27
10% Ringold clay 90% Glaciofluvial sand	0.78	0.46	0.63
50% Ringold clay 50% Glaciofluvial sand	0.54	0.37	?

*Model plug left for 12 hours in basalt block in oven at 100°C prior to testing. Bond strength values are approximate and are obtained from pressure gauge indication of a hydraulic jack.

- In general, the contamination of the simulated borehole walls in the basalt core produced a decrease in bond strength. Percent deterioration was found to be greater for higher clay content; and
- Experimental values for bond strength obtained at high temperature (100°C) indicated a net deterioration of the bond for a clay content of 50 percent. This may be due to shrinkage of the clay fraction in the compacted soil plug; testing at high temperature was made without attempting to maintain moisture content in the plug.

An exceptionally high bond strength (7 MPa) was observed for bentonite/sand mixtures containing 90 percent glaciofluvial sand. In this test, the miniature plug/basalt host rock models were left for 12 hours in a conventional oven at 100°C prior to testing. Accordingly, no comparison of bond strengths was attempted between mixtures containing various percentages of clay because different curing methods were applied. Note that bond strengths obtained for bentonite mixtures containing 90 percent sand were approximately twice those observed for grout plug/basalt (host rock) models at high temperature (see Section 5.5.3.3). These high bond strengths are significant and may be the result of cementation between the basalt core walls and the compacted soil plug. Further testing is strongly recommended to confirm this result.

5.6.3.2 Permeability of Compacted Soil Plug/Basalt (Host Rock) Models

Saturation time and permeability results are given in Table XXIII for the compacted soil plug/basalt (host rock) models. Only one permeability test was completed within the

TABLE XXIII
SUMMARY OF PERMEABILITY TESTS ON
COHESIVE PLUG/BASALT (HOST ROCK) MODELS

MIXTURE COMPONENTS	SATURATION TIME (DAYS)	PERMEABILITY (cm/sec)
10% Wyoming bentonite 90% Glaciofluvial sand	42	Still saturating
50% Wyoming bentonite 50% Glaciofluvial sand	53	Still saturating
10% Oregon bentonite 90% Glaciofluvial sand	37	9.5×10^{-8}
50% Oregon bentonite 50% Glaciofluvial sand	62	Still saturating
50% Ringold clay 50% Glaciofluvial sand	38	Still saturating

NOTES: Plug volume = $2.32 \times 10^{-4} \text{ m}^3$
Hydraulic gradient = 4

time limit of the physical testing program. A model plug composed of 10 percent Oregon bentonite and 90 percent glaciofluvial sand was observed to have a permeability of 9.5×10^{-8} cm/sec. This value is somewhat higher than that desired in laboratory testing of permeability, which should be near the permeability reported for intact basalt (Table A-I, Appendix A). Actual field placement of a similar plug in a borehole, shaft, or tunnel should result in a still higher in-situ permeability.

The four other permeability model tests were still not completely saturated by the end of this testing program. In the case of mortar or concrete plugs, saturation times varied between one and two weeks for permeabilities less than 10^{-8} cm/sec. Saturation times for soil plugs composed of 10 percent Oregon bentonite and 90 percent glaciofluvial sand were more than twice as long (four weeks) for a sample having a permeability almost 10 times greater. This clearly shows the slowness of the hydration process in bentonite mixtures. For the mixture having 10 percent Wyoming bentonite and 90 percent glaciofluvial sand, 42 days were insufficient to obtain complete saturation of the model plug.

In some respects, soil consolidation theory governing the displacement of excess pressured water out of clay samples may be representative of the mechanisms governing the movement of excess pressured water into an unsaturated sample. Rough calculations with such a theory suggest 50 days of saturation time is not excessive. Furthermore, similar calculations show that a 7-m diameter prototype plug of compacted Wyoming bentonite and sand (with a clay content of 50 percent) may require more than 1,000 years to achieve saturation. Furthermore, clay/sand mixtures with 50 percent Wyoming

bentonite are expected to be essentially impervious, as stated by Grim (1962), although no experimental data are available to confirm this. These observations confirm the relatively good performance of compacted clay/sand plugs as seepage barriers.

5.6.3.3 Consolidation Tests on Compacted Sand/Clay Mixtures

Curves showing variations in void ratio with variations in consolidation pressure are given in Figures 38 and 39 for Oregon bentonite/glaciofluvial-sand mixtures having clay contents of 10 and 50 percent. Oregon bentonite mixtures with a clay content of 10 percent had a low compressibility. Under consolidation pressures ranging from 3 to 6.4 MPa, the compression index was only 0.02. However, the unloading part of the consolidation curve exhibits a hysteresis that suggests the potential for separation at the interface between the soil plug and borehole wall after cyclic loading. Such cyclic loading could be produced by thermal cycles in the repository environment due to radioactive waste decay.

By contrast, the Oregon bentonite mixture with a clay content of 50 percent exhibited a higher compressibility; a compression index of 0.105 was computed for consolidation pressures ranging from 3 to 6.4 MPa. However, in this case the unloading part of the consolidation curve indicates a strong swelling potential for this mixture. Void ratio values more than or equal to the initial void ratio of the compacted mixture were observed for consolidation pressures less than or equal to 3 MPa during loading and less than or equal to 2.2 MPa during unloading. This result suggests that, even after cyclic loading, a tight contact between the soil plug and borehole wall should be expected. For unloading pressures less than 2.2 MPa, the confined plug should even exert a self-stressing pressure against the walls due to swelling of the plug material. This

EXPLANATION e_i = Initial void ratio e_f = Final void ratio C_c = Compression index (for loading pressure ranging from 3.2 to 6.4 MPa)**FIGURE 38**

CONSOLIDATION CURVE OF CLAY/SAND MIXTURES CONTAINING
10% OREGON BENTONITE AND 90% GLACIOFLUVIAL SAND

EXPLANATION e_i = Initial void ratio e_f = Final void ratio C_c = Compression index (for loading pressure ranging from 3.2 to 6.4 MPa)**FIGURE 39**

CONSOLIDATION CURVES OF CLAY/SAND MIXTURES CONTAINING
50% OREGON BENTONITE AND 50% GLACIOFLUVIAL SAND

result is considered promising but should be confirmed and extended by testing the long-term swelling potential of sand/clay mixtures under elevated temperature conditions.

5.7 SOIL/CLAY SLURRIES - PERFORMANCE TESTS

As discussed in Section 5.4, the primary objective of evaluating clay slurries was to determine the most suitable slurry for use in conjunction with crushed basalt gravel. Such material would derive its strength from a framework of crushed basalt in grain-to-grain contact; the slurry would be intruded into framework voids to act as an impermeable filler which would inhibit fluid migration as well as adding to the ion exchange potential and sorption capacity of this type of plug material. On the basis of workability, stability and thixotropy evaluated for various candidate clays during screening tests (Section 5.4), only those slurries containing 6 to 8 percent by weight of premium grade bentonite (Shurgel) were found to be suitable.

Premixed combinations of clay slurries and gravel or coarse-crushed basalt should have the same low permeability, enhanced ion exchange potential, and sorption capacity as slurry/aggregate mixtures produced by injection of a slurry into a coarse granular framework. Premixed materials make it possible to use slurries containing sand and natural clay that were found to be unsuitable for slurry injection during screening tests and, thereby, allow for a wider variety of plug materials. The sand and clay can occupy a significant portion of the void space between coarse gravel or basalt aggregate as well as be incorporated into the grain-to-grain contacts of the structural framework itself. Consequently, the relative proportions of components in premixed slurry/aggregate samples can be more varied than for slurry injection samples

5.7.1 Design of Materials and Mixtures

As was discussed in Section 5.4.3, a slurry containing 6 to 8 percent by weight Shurgel (processed bentonite) was found to exhibit the best properties of workability, stability, and thixotropy. Therefore, this slurry was adopted for further study in this phase of physical testing and was combined with fine-crushed zeolite (-4.6 mm) from Oregon, Ringold clay D, and precompressed bentonite pellets to form a variety of samples. Crushed basalt gravel (-1.9 cm) used in these tests was from the Hanford Site.

Test mixtures are listed in Tables XXIV and XXV. Percentages listed on these tables indicate percentage of solids by weight. All materials, except Shurgel, were mixed in an air-dried condition. Shurgel was prepared as a slurry that contained the percent solids by weight given in parenthesis on Tables XXIV and XXV.

The following rationale was used in developing each of these mixtures:

- For samples PT 428 I, II, and III, air-dried gravel was packed as densely as possible; slurry was then injected into the sample;
- For sample PT 429 A, air-dried gravel was premixed with slurry containing bentonite pellets to determine if the hydration and swelling of the pellets would offset, or even exceed, consolidation of the mixture;

TABLE XXIV
Summary of Data and Test Results for Preplacement and Slurry Injection of Aggregate

Mixture	Density	Porosity	Bond Strength
PT 428 I ^a 98% Crushed basalt gravel 2% Shurgel (7% slurry)	Sample volume = 409.75 cm ³ Dry density of aggregate = 1.46 gm/cm ³ = 39% relative density Density of slurry = 1.009 gm/cm ³ Initial sample density = 1.95 gm/cm ³ (questionable data)	Assume G _{Basalt} = 2.84; G _s = 0.98(2.84) + 0.02(2.75) G _{Shurgel} = 2.75; G _s = 2.84 Since Sample density = [n + (1 - n)G _s]γ _u 1.95 gm/cm ³ = [n + (1 - n) 2.84](1.0 gm/cm ³) Therefore n = 0.48	<ul style="list-style-type: none"> ● Sample slumped out of steel mold. ● Rubber membranes were not used inside steel mold.
PT 428 II ^a 98% Crushed basalt gravel 2% Shurgel (7% slurry)	Sample volume = 419.09 cm ³ Dry density of aggregate = 1.54 gm/cm ³ = 68% relative density Density of slurry = 1.010 gm/cm ³ Initial sample density = 1.95 gm/cm ³	Assume as above, G _s = 0.98(2.84) + 0.02(2.75) G _s = 2.84 Since 1.95 gm/cm ³ = [n + (1 - n) 2.84](1.0 gm/cm ³) Therefore n = 0.48	<ul style="list-style-type: none"> ● Sample slumped out of steel mold after plug resistance reached 0.002 kg/cm². ● Rubber membrane was not used inside steel mold.
PT 428 III ^b 98% Crushed basalt gravel 2% Shurgel (7% slurry)	Sample volume = 378.66 cm ³ Dry density of aggregate = 1.63 gm/cm ³ = 100% relative density Density of slurry = 1.033 gm/cm ³ Initial sample density = 2.07 gm/cm ³	Assume as above, G _s = 0.98(2.84) + 0.02(2.75) G _s = 2.84 Since 2.07 gm/cm ³ = [n + (1 - n) 2.84](1.0 gm/cm ³) Therefore n = 0.42	<p>No test possible</p> <ul style="list-style-type: none"> ● Rubber membrane was used inside steel mold. ● Triaxial compressive strength test pending.

^aNo test for permeability or compressibility.

^bNo test for permeability. Compressibility:

Initial sample heights = 13.2 cm under an effective consolidation pressure of 4 kg/cm².

Sample height had decreased by 1.55 mm when measured after a period of 19 days. If sample diameter also decreased

$$\frac{\Delta D}{D} = \frac{\Delta L}{L}$$

$$\text{then } \Delta D = 5.9 \text{ cm } \frac{0.155}{13.2} \\ = 0.07 \text{ cm}$$

then volume decreased also

$$V' = \frac{\pi}{4}(D-\Delta D)^2 (L-\Delta L)^2 \\ = 348 \text{ cm}^3$$

and the amount of volume change (ΔV) is:

$$V - V' = 361 \text{ cm}^3 - 348 \text{ cm}^3 = 13 \text{ cm}^3$$

TABLE XXV

SUMMARY OF DATA AND TEST RESULTS FOR PREMIXED SLURRY AND AGGREGATE

Mixture	Density	Porosity	Compressibility
PT 429A ^a 89% Crushed basalt gravel 9% Bentonite pellets 2% Shurgel (7% slurry)	Sample weight = 1,188 gm Initial sample volume = $\frac{\pi}{4}(10.4 \text{ cm})^2(7.24 \text{ cm})$ = 615.21 Initial density = $\frac{1,188 \text{ gm}}{615.21 \text{ cm}^3}$ = 1.93 gm/cm ³	Assume G _{Basalt} = 2.84 G _{Pellets} = 1.84 G _{Shurgel} = 2.75 $G_s = 0.89(2.84) + 0.09(1.84) + 0.02(2.75)$ $G_s = 2.75$ Since Sample density = $[n + (1 - n) G_s]$ $1.93 \text{ gm/cm}^3 = [n + (1 - n) 2.75]$ $\times (1.0 \text{ gm/cm}^3)$ Therefore $N = 0.47$ $e = 0.89$	Initial sample volume = 615.21 cm ³ Cumulative change in sample volume = 8.68 cm ³ over a period of 2 $\frac{1}{2}$ days (effective pressure = 5 kg/cm ²) When sample removed from mold, a significant amount of bentonite had still not hydrated. During the 22-day period the change in sample volume involved: 26.06 cm ³ of swelling, and -34.74 cm ³ of compression
PT 429 B 20% Crushed basalt gravel 45% Crushed zeolite 27% Ringold clay 8% Shurgel (8% slurry)	Sample weight = 986 gm Initial sample volume = $\frac{\pi}{4}(10.41 \text{ cm})^2(7.11 \text{ cm})$ = 605.30 cm ³ Initial density = $\frac{986 \text{ gm}}{605.30 \text{ cm}^3}$ = 1.63 gm/cm ³	Assume G _{Basalt} = 2.84 G _{Pellets} = 2.51 G _{Ringold} = 2.70 G _{Shurgel} = 2.75 $G_s = 0.2(2.84) + 0.45(2.31) + 0.27(2.70) + 0.08(2.75)$ $G_s = 2.56$ Since $1.63 \text{ gm/cm}^3 = [n + (1 - n) 2.56]$ $\times (1.0 \text{ gm/cm}^3)$ Therefore $N = 0.60$ $e = 2.0$	Initial sample volume = 605.30 cm ³ Under an effective pressure of 5 kg/cm ² Sample volume decreased by 40.15 cm ³ over a period of 825 minutes; thereafter, no significant change in sample volume occurred since the loading platen was now sitting on the steel mold.
PT 429C ^b 50% Crushed basalt gravel 25% Crushed zeolite 19% Ringold clay 6% Shurgel (8% slurry)	Sample weight = 1,100 gm Initial sample volume = $\frac{\pi}{4}(10.41 \text{ cm})^2(7.57 \text{ cm})$ = 644.21 cm ³ Initial density = $\frac{1,100 \text{ gm}}{644.21 \text{ cm}^3}$ = 1.71 gm/cm ³	Assume $G_s = 0.5(2.84) + 0.25(2.31) + 0.19(2.70) + 0.06(2.75)$ $G_s = 2.68$ Since $1.71 \text{ gm/cm}^3 = [n + (1 - n) 2.68]$ $\times (1.0 \text{ gm/cm}^3)$ Therefore $N = 0.58$ $e = 1.38$	Initial sample volume = 644.21 cm ³ under the influence of an effective pressure of 4.5 kg/cm ² . Sample volume decreased by 37.85 cm ³ after a period of 101 minutes, then decreased by 10.65 cm ³ over the next 3,844 minutes; the sample was then unloaded, readjusted, and reloaded which produced a decrease in sample volume of 33.27 cm ³ over a period of 2,850 minutes. No further change occurred thereafter.
^a Channeling of sample due to particle migration, no test possible for permeability. ^b Using effective pressure of 0.98 MPa, back pressure = 0.51 MPa, and K = 1.2 x 10 ⁻⁸ cm/sec.			

- For sample PT 429 B, a fine aggregate of crushed zeolite and Ringold clay was added to gravel and slurry to determine if the addition of these would decrease the mixture's permeability; and
- For sample PT 429 C, a different ratio of coarse aggregate to fine aggregate was used to determine what effect this ratio had on the permeability and consolidation of mixtures.

5.7.2 Tests and Procedures

The original intention of these studies was to test slurry/aggregate mixtures where the samples were prepared by injecting slurry into a coarse matrix. A special mold for sample preparation was developed which produced samples that could be placed in a conventional triaxial pressure cell for permeability and compressive strength tests. This sample preparation procedure allowed a sample to be subjected to isotropic consolidation while simultaneously performing a falling head permeability test on the same sample and then failing the sample in triaxial compression. This procedure was followed for sample PT 428 III (see Table XXIV); samples PT 428 I and II represent attempts to measure the bond strength developed between slurry/aggregate mixtures and the steel, sample preparation mold.

When testing was later expanded to include samples of premixed slurry and aggregate, there was no time to develop laboratory equipment which could test these mixtures in a manner identical to the conventional triaxial tests used on mixtures prepared by slurry injection. However, equipment in the WCC laboratory in Oakland, California, was available to modify a triaxial

pressure cell with a steel consolidometer so that samples could be premixed, placed in the consolidometer, and then subjected to one-dimensional consolidation while simultaneously performing a falling head permeability test.

It is important to note that the procedures used to test the two types (injection versus premixed) of slurry/aggregate mixtures were significantly different. Slurry injection samples were isotropically consolidated within a rubber membrane. However, the premixed slurry/aggregate samples were one-dimensionally consolidated within a steel consolidometer. In the case of slurry injection samples, the rubber membrane squeezing the sample intruded void spaces around the sample perimeter and altered the cross-sectional area of the sample itself. On the other hand, the steel consolidometer maintains a constant cross-sectional area, and contact conditions with the sample are different. Consequently, the two types of slurry/aggregate mixtures were not only consolidated differently, conditions around the sample perimeter during permeability tests were also significantly different for the two types of samples.

5.7.3 Test Results and Discussion

A summary of data and test results for slurry injection samples is given in Table XXIV, and a summary for premixed slurry/aggregate samples is given in Table XXV. Both tables use the same format, but procedures used to obtain data and test results were significantly different, as discussed above. Thus, caution must be exercised when comparing data from one table with data from the other. However, if used with care, the data and results are still considered a legitimate basis for reasonable comparisons and valid conclusions.

5.7.3.1 Bond Strength for Slurries

The two attempts at determining the bond strength of slurry/aggregate mixtures that involved injection proved futile. In both instances, the sample essentially slumped out of the steel mold under the influence of its own weight, indicating that little cohesive or frictional force was available to resist sample movement. The lack of cohesion was attributed to the inability of the Shurgel clay particles to interact with the walls of the mold, while the lack of significant granular frictional resistance on the wall was attributed to the low relative density of the aggregate as well as the lubrication of aggregate particles when coated with slurry. However, this lack of cohesion and friction was not exhibited by the samples themselves because they were capable of supporting their own weight when the split steel mold was disassembled from around them.

Some important observations on strength characteristics were made when a sample of premixed slurry and aggregate (sample PT 429I, Table XXV) was removed from the steel consolidometer. This sample was essentially the same composition as slurry injection samples, except that it contained bentonite pellets and had undergone a period of consolidation. Due to swelling of the bentonite and simultaneous consolidation, the sample was tightly squeezed within the steel consolidometer; it did not slump out of the container under the influence of its own weight as other similar samples had. This sample was, in fact, difficult to dig out of the container. In addition, bonding between gravel grains was significantly greater than that exhibited by samples prepared by slurry injection. It appears that hydration and swelling of the bentonite pellets, in

conjunction with sample consolidation, had an important influence on the cohesive strength of the mixture.

5.7.3.2 Compressibility of Clay Slurries

From test results shown in Tables XXIV and XXV, inconsistencies resulted due to problems with maintaining pressures and measuring changes in sample height. However, general data trends indicate that compressibility of the various mixtures increased with increasing porosity. With respect to sample PT 429A (Table XXV), the relationship between porosity and compressibility is difficult to evaluate because test results were strongly influenced by swelling of the bentonite pellets. The volume changes experienced by this sample alternated between swelling and compression, in part due to the bentonite and in part due to the cell pressure regulator which allowed the effective consolidation pressure to fluctuate between 0.1 and 0.48 MPa. However, the capacity of bentonite to swell did appear to offset the effect of consolidation.

Test results for premixed slurry/aggregate samples PT 429 B and PT 429 C indicate that an increase in the percentage of fine aggregate will produce an increase in porosity and an attendant increase in compressibility. In addition to the high porosity of these mixtures (which, in turn, affects compressibility), D'Appolonia and Ryan (1979) present data showing that compressibility of a slurry/aggregate mixture will also increase as the percentage of coarse aggregate (structural framework) is decreased. One other consideration, mentioned earlier, is the low strength and breakdown of crushed zeolite, which will also increase the compressibility of mixtures.

5.7.3.3 Permeability of Clay Slurries

As shown on Tables XXIV and XXV, only one permeability test was fully completed. The sample (PT 429 C) incorporated premixed slurry, coarse aggregate, and fine aggregate that was consolidated under an effective pressure of 0.45 MPa and then subjected to a falling head permeability test with the effective pressure reduced to 0.1 MPa. The coefficient of permeability was determined to be 10^{-8} cm/sec, which is consistent with results presented by D'Appolonia and Ryan (1979) for such a mixture.

Special note should be made of a problem which arose when sample PT 429 A (Table XXV) was being consolidated prior to a permeability test. The sample was connected to hydraulic pressure lines that allowed water at a back pressure of 0.4 MPa to flow through the sample under the influence of a differential pressure of approximately 0.025 MPa. Filter paper had been placed on top of the sample to prevent particle migration out of the sample under the influence of seepage forces. Unfortunately, a fold developed in the filter paper, particle migration occurred, and a small channel developed through the sample. Once this small channel formed, water began flowing through it essentially unimpeded, and erosion of fine particles from the sample occurred. Thus, it would appear that particle migration and channeling of slurry/aggregate mixtures is a very real possibility and must be given serious consideration when dealing with these mixtures in plug design schemes.

5.7.3.4 Summary of Results for Clay Slurries

Based on preliminary test results for clay slurries, the following conclusions were made:

- The bond strength of a slurry/aggregate mixture was greatly enhanced when bentonite pellets were added and the mixture was subjected to consolidation;
- Compressibility of a slurry/aggregate mixture increased as its porosity increased and percent coarse aggregate decreased;
- For slurry mixtures containing 6 percent bentonite by weight, the permeability should be on the order of 10^{-8} cm/sec; and
- It appears that channeling (piping) of slurry/aggregate mixtures can develop rapidly once particle migration has been initiated and should be taken into consideration in preconceptual plug design schemes.

5.8 SUMMARY OF THE PHYSICAL TESTING PROGRAM

5.8.1 Preferred Materials

A preliminary evaluation of the suitability of materials and mixtures for further testing and evaluation in preconceptual plug design can be made based on the results of the physical testing program. However, final design criteria defining the performance limits of a suitable plug system and long-term tests (which include the simulation of critical thermomechanical and hydrological in-situ conditions) are

needed prior to the final selection of materials for plug design. Nonetheless, quantitative experimental data collected during the physical testing program provide guidelines for recommending the suitability of various candidate materials at this time. A description of candidate materials included in this discussion of suitability is given for: (1) cements plus their additives (Table XXVI); (2) cohesive materials (Table XXVII); and (3) non-cohesive granular materials (Table XXVIII).

5.8.1.1 Cements Plus Cement Additives

On the basis of these studies, portland cement Type V is the preferred cement for use in plugs; it combines high sulfate resistance with an acceptable mechanical performance. The addition of a finely ground, high-silica pozzolan to portland cement is recommended and was found to reduce shrinkage, increase workability, improve impermeability, and increase stability of cement mixtures exposed to moderate temperature (less than 100°C). The addition of a finely ground silica flour to portland cements was found to reduce the shrinkage and substantially improve thermal stability and structural strengths of cement mixtures exposed to temperatures greater than 100°C.

TXI Chem Com cement and portland pozzolan cement combine low shrinkage with good structural strength when cured at standard temperatures. However, they show a substantial deterioration when cured at elevated temperatures, and their chemical resistance to sulfate attack still needs to be demonstrated.

Secar (calcium aluminate cement) and portland cement Type II may be acceptable, although performance tests did not equal that of portland cement Type V. In addition, their high demand

TABLE XXVI

SUITABILITY OF CEMENTS AND ADDITIVES BASED ON PHYSICAL TESTING

<u>Materials</u>	<u>Description</u>	<u>Suitability</u>
Portland cement Type II	Moderate sulfate resistant	Less stable and lower structural strength than Portland Type V cement.
Portland cement Type V	High sulfate resistant	<u>Recommended</u>
Portland pozzolan cement	Portland Type I-II cement + Gypsum + 15% of finely ground expanded shale	Low shrinkage, high strength at low temperature. Significant loss in structural strength at high temperature. Sulfate resistance has to be tested.
Fondu cement	Calcium aluminate cement with high early strength	High heat of hydration, difficult to handle. Significant loss in structural strength at high temperature.
Secar cement	Calcium aluminate cement with high early strength	Quite stable at high temperature. Low shrinkage. High water/cement ratio for a given consistency. Relatively low structural strength.
TXI Chem Com	Expansive cement	Low shrinkage, high strength at low temperature. Significant loss in structural strength at high temperature. Sulfate resistant has to be tested.
Lassenite (pozzolan)	Calcined volcanic ash	<u>Recommended</u> as additive in portland cement mixtures for moderate temperature locations $T < 100^{\circ}\text{C}$.
Silica flour	-325 Mesh silica powder	<u>Recommended</u> as additive in portland cement mixtures for high temperature locations $T \geq 100^{\circ}\text{C}$
Plastiment	Water-reducing retarder agent (hydroxylated carboxylic acid)	<u>Recommended</u>
Aluminium powder	-200/+325 Mesh and -325 Mesh (unpolished)	Poor reactivity as a gas-forming agent
Aluminium powder	-325 Mesh (polished, leafing type)	<u>Recommended</u>

TABLE XXVII

SUITABILITY OF COHESIVE MATERIALS BASED ON PHYSICAL TESTING

<u>Materials</u>	<u>Description</u>	<u>Suitability</u>
Ringold clay Unit A	Inorganic clay with high plasticity	Poor availability
Ringold clay Unit B	Inorganic silt with low compressibility	Low plasticity
Ringold clay Unit C	Inorganic clay with medium plasticity	Low compactibility
Ringold clay Unit D	Inorganic clay with high plasticity	<u>Recommended</u> as second choice for compacted backfill
Ringold clay Unit E	Inorganic clay with high plasticity	Slight homogeneity
Ringold clay Unit F	Silt	Non-plastic
Touchet Formation	Inorganic silt with low compressibility	Low plasticity
Oregon bentonite	Montmorillonite clay	<u>Recommended</u> as first choice for compacted backfill
Wyoming bentonite	Montmorillonite clay	<u>Recommended</u> as first choice for compacted backfill
Shurgel	Processed bentonite	<u>Recommended</u> for bentonite slurries
Aquagel	Processed bentonite	Develops slightly lower viscosity than Shurgel when mixed with water.
Bentonite pellets	1.25 cm diameter, highly compacted spherical pellets.	<u>Recommended</u>

TABLE XXVIII

SUITABILITY OF NON-COHESIVE MATERIALS, BASED ON PHYSICAL TESTING

<u>Materials</u>	<u>Description</u>	<u>Suitability</u>
Glaciofluvial sand	Washed sand from the Hanford Site	<u>Recommended</u> in cementitious and compacted earth mixtures.
Crushed basalt sand	Crushed, dense, and sound basalt from the Hanford Site	<u>Recommended</u> in cementitious and compacted earth mixtures.
Crushed zeolite sand	Clinoptilolite from eastern Oregon	Weak and porous aggregate with a high ion exchange potential; recommended for non-optimum plug backfill.
Crushed gravel	-2.5 cm crushed gravel from the Hanford Site	<u>Recommended</u> in cementitious mixtures.
Crushed basalt gravel	-1.9 cm coarse-crushed basalt sand from the Hanford Site	<u>Recommended</u> in cementitious, compacted earth and premixed clay slurry mixtures.

for water to achieve a given consistency may produce relatively high permeabilities in the final products. Fondu (calcium aluminate cement) is not recommended; it was initially chosen as a candidate cement for high temperature locations but was found to have a high heat of hydration for a short time of set. This could lead to in-situ placement difficulty. It also undergoes a significant decrease in structural strength when exposed to an elevated curing temperature.

From among the three types of aluminum powder that were tested, the polished, leafing-type showed far more reactivity as a gas-forming agent than did the two unpolished types. The addition of a WRA, Plastiment, in cement mixtures was found to effectively reduce water demand, improve workability of freshly mixed cement, and slightly increase structural strength and density of hardened mixtures.

5.8.1.2 Cohesive Materials

Bentonite clay is recommended for use in compacted clay/sand or skip-graded clay/sand/aggregate mixtures. Its extreme plasticity (indicative of a very low permeability) and high ion exchange potential and sorption capacity should substantially help to decrease both fluid and radionuclide migration through plugs. The high swell potential of bentonite should result in a tight closure between the plug and wall rock. Bentonite is also expected to provide some self-healing capacity to plug mixtures and to fill wall rock fractures. On the basis of this study, a slight preference is given to Wyoming bentonite because of its somewhat higher plasticity and greater compactability when compared to Oregon bentonite. Of the seven fine-grained clay samples from the Pasco Basin that were tested, Ringold clay D may be the only satisfactory material

for use in plugs. The performance of other clay materials was found to be superior to Ringold clay D; the recommendation at this time is to limit its use to general applications and to not use it in high-performance plugs.

From among candidate bentonite samples, Shurgel was found to have the best gel strength in slurry mixtures. Gel strength evaluations at ambient temperature indicate that a clay/water ratio of 7 percent produces the most efficient pumpability and most acceptable thixotropy in slurries. The use of precompacted bentonite pellets in premixed slurry/aggregate samples appeared to increase cohesion and bond strength with the wall rock after consolidation of the mixture. Further tests are needed to verify this result.

5.8.1.3 Non-Cohesive Granular Materials

Fine and coarse-crushed basalt samples collected from the Umtanum and other lower basalt flows, and glaciofluvial sand and gravel collected from the Hanford Site, are strong, competent granular materials; they are recommended for use as aggregate in cementitious mixtures, in compacted earth materials, and in premixed clay slurries containing aggregate. Crushed zeolite samples had low unit weights, low specific gravity, and very high porosity. Because of the high ion exchange potential and sorption capacity of zeolite, crushed zeolite is recommended for use only in compacted backfill.

5.9 CONCLUSIONS AND RECOMMENDATIONS

At this time, concrete, grout, compacted earth materials, and clay slurries are all considered feasible materials for sealing man-made accesses to a repository in basalt. Tests conducted

during this study evaluated the permeability and bond strength of miniature plug/basalt (host rock) models at low and high temperatures. These tests indicate that the design mixtures of candidate plug materials that have permeabilities of less than 10^{-8} cm/sec and that will form acceptable bond strengths with the host rock are possible. Other major conclusions are:

- The addition of finely ground silica flour greatly improves the structural and bond strength of portland cement cured at elevated temperature; it also reduces shrinkage of portland cement mixtures cured at standard temperature;
- Compaction test results for bentonite/sand mixtures indicate that compaction to produce a relatively impervious clayey mixture is feasible by standard compactive methods;
- Significant time is required for a miniature, simulated compacted bentonite/sand plug to hydrate. On the basis of test data and theoretical considerations, the time required to saturate a 7-m diameter compacted bentonite/sand plug with a clay content ratio of 50 percent may be more than 1,000 years;
- Consolidation test results for bentonite/sand mixtures with a clay content of 50 percent indicate an expansive behavior in these mixtures for unloading pressures less than 2.2 MPa. These results suggests a high swelling potential and self-healing properties for plugs composed of these materials. The results also suggest that tight contact between the plug and basalt (host rock) will be maintained even after cyclic thermal loading; and

- Mud contamination of simulated borehole walls during model testing was found to substantially decrease the bond strength of miniature cement and soil plugs with the basalt (host rock), which strongly suggests that drilling mud should be flushed from boreholes before plugging.

Results of the physical testing program point to promising areas of future study that would require extensive experimental investigations to obtain additional conclusive and useful quantitative information. The promising areas most recommended for future study are:

- The potential for cementation between the basalt (host rock) and compacted bentonite/sand mixtures at high temperature. This study is suggested by the exceptionally high bond strengths observed for soil plug/basalt (host rock) models cured at high temperature; and
- The retardation of the hydration and swelling processes of bentonite pellets in slurries. This retardation resulted in a significant increase in cohesion and bond strength between premixed bentonite slurries containing aggregate and the host rock upon consolidation of the slurries.

6 SUITABILITY OF MATERIALS FOR USE IN PRECONCEPTUAL PLUG SYSTEMS

6.1 INTRODUCTION

The main objective of the geochemical and physical testing programs discussed in the previous two chapters was to help assess the suitability of preferred candidate plug materials selected by the process described in Taylor and others (1979), and in Chapter 3 of this report. These programs were designed to screen materials from the preferred list (Table I) and select those which continued to show the greatest promise for meeting the initial requirements of preconceptual plug designs and compatibility with the natural environment at the Hanford Site (and with alterations to that environment produced by excavation of the repository).

Both testing programs used essentially the same set of samples prepared from the list of preferred candidate materials. The geochemical program examined reaction rates of individual materials in simulated ground water (similar to that expected to exist at the depths of plug seats on the Hanford Site) and the reaction rates of mixtures of candidate materials in simulated ground water. The tests were performed under a variety of temperatures and pressures designed to maximize (and in most cases accelerate) potential reactivity between the various components.

The physical testing program combined the candidate plug materials (using various grain sizes and proportions) in mixtures that are precursors to actual plug designs. These tests were, again, designed as a screening step to select those individual materials and mixtures that exhibited the most

desirable performance when submitted to a wide variety of mechanical and physical test sequences. The results of these two testing programs (Sections 4.5, 4.6, and 5.8) are combined in the following discussion of suitability and preference for materials to be used in preconceptual plug designs and plug systems.

6.2 SUITABILITY OF MATERIALS BASED ON TESTING PROGRAMS

As indicated in Chapter 4, on the basis of geochemical testing, all preferred candidate plug materials are considered suitable for further testing and use in preconceptual plug design. Small differences in relative reactivity were noted for the various samples, but the reactivities of all test samples were so low that all are considered acceptable. The self-cementing characteristics of basalt under hydrothermal test conditions give this material an added degree of desirability at this stage of evaluating plug materials.

A list of preferred material mixtures, designed and tested during the physical testing program for preconceptual plugging systems, is given in Table XXIX. In this table, the components and proportioning data used in constructing these preferred samples during the physical testing program are also tabulated. The mixtures listed in Table XXIX are the same as those tested in the geochemical testing program. At this stage, data on mixture proportions are flexible and approximate; they need to be confirmed and refined by further advanced testing. Seven preferred mixtures are proposed as most suitable for sealing man-made accesses to a nuclear waste repository in basalt.

TABLE XXIX

PREFERRED MATERIAL MIXTURES FROM THE RESULTS OF PHYSICAL TESTING

<u>Type of Mixtures</u>	<u>Compound Description</u>	<u>Proportioning Data</u>		<u>Comments</u>
Cement grout Moderate temperature Location ($T < 100^{\circ}\text{C}$)	Portland Type V Lassenite ^a Glaciofluvial sand Aluminum powder Plastiment ^b Water	602 kg 241 kg 723 kg 180 g 125 ml 447 liters	mix design per m ³ of concrete and grout mixtures	Refinement in proportioning data needed to obtain a non-shrink grout
Cement grout High temperature Location ($T \geq 100^{\circ}\text{C}$)	Portland Type V Silica flour Glaciofluvial sand Aluminum powder Plastiment Water	586 kg 315 kg 772 kg 176 g 122 ml 414 liters		
Concrete Moderate temperature Location ($T < 100^{\circ}\text{C}$)	Portland Type V Lassenite Glaciofluvial sand Crushed gravel Plastiment Water	273 kg 55 kg 755 kg 1,132 kg 686 ml 174 liters		Water cement ratio can be reduced to obtain a 7.5 cm slump
Concrete High temperature Location ($T \geq 100^{\circ}\text{C}$)	Portland Type V Silica flour Glaciofluvial sand Crushed gravel Plastiment Water	289 kg 156 kg 709 kg 1,063 g 931 ml 179 liters		
Compacted clay/sand mixture in confined plug	Wyoming bentonite Glaciofluvial sand	Clay/sand ratio ranging from 0.3 to 0.5		Permeability test data needed
Compacted clay/sand mixture in confined plug	Oregon bentonite Glaciofluvial sand	Clay/sand ratio around 0.3		Permeability test data needed
Slurry/aggregate mixture in confined plug	Shurgel (7% in slurry) bentonite pellets coarse-crushed basalt	Clay/pellets/ aggregate ratio 0.02/0.09/0.89		Permeability bond strength test data needed
^a Lassenite (brand name) is a natural pozzolan. ^b Plastiment (brand name) is an organic water reducing agent in cements.				

Note that these mixtures may not be acceptable as single materials in a monolithic plug system. For example, the use of a high silica pozzolan in portland cement Type V mixtures is only recommended for temperatures less than 100°C, while the use of silica flour was found to be beneficial in portland cement mixtures exposed to temperatures of 100°C or more. In addition, permeability tests are still needed to develop precise proportioning data on compacted bentonite/sand mixtures. However, testing to date has shown that a minimum of 30 percent bentonite by weight is needed to obtain low permeabilities in these mixtures. This percentage is also an upper limit at which good compactibility of the Oregon bentonite/sand mixture can be obtained. By contrast, in compacted Wyoming bentonite/sand mixtures, acceptable compaction was observed with clay contents as high as 50 percent. Considering the high percentage of bentonite required for the desired hydraulic performance, the use of compacted clay/sand mixtures is recommended primarily for multizone plug systems where confinement is provided by a rigid material capable of having good structural strength. This limitation is also valid for premixed aggregate clay slurries that will require confinement in order to prevent channeling or piping of plug materials.

6.3 MATERIALS PREFERRED FOR PRECONCEPTUAL DESIGN AND FURTHER TESTING

The results of the geochemical and physical testing indicate that the materials considered suitable for further testing and use in preconceptual design schemes are various combinations of compacted natural materials, grouts, and concretes. Geochemical testing in the hydrothermal test conditions employed during laboratory testing at SRI shows that the

materials are generally non-reactive or have low reactivities, which suggests stability in the proposed plug environment. Table XXIX summarizes the physical test results and shows the preferred combinations and proportions of potential plug components that exhibited desirable behavior during test runs. The major plug components considered most suitable on the basis of the laboratory testing are listed on Table XXX. Also included on Table XXX are those additives that were incorporated into the testing programs and that produced improved behavior and mechanical response in mixtures during physical testing.

TABLE XXX
MATERIALS DETERMINED TO BE MOST SUITABLE
FOR FURTHER STUDY

<u>Major Component Plug Material</u>	<u>Tested Additive</u>
Basalt	Lassenite ^a
Glaciofluvial sand (in cement)	Plastiment ^b
Oregon bentonite	Aluminum powder
Wyoming bentonite	Silica flour
Crushed gravel (in cement)	
Portland Type V cement	
Zeolite ^c	

^aLassenite (brand name) is a natural pozzolan.
^bPlastiment (brand name) is an organic water-reducing agent in cements.
^cZeolite is considered usable for backfill purposes on the basis of physical testing; however, it has marginal strength when placed in mixtures. Its known properties (ability to inhibit radionuclide migration and chemical compatibility with the natural environment) make it desirable for use in some applications in plug design. Further testing is needed.

7 LIMITATIONS OF THE RESULTS

Each of the previous five chapters represents a significant step in establishing design limits and selecting materials for preconceptual plugs and systems. However, limitations exist on the uses of the data and results presented in this report.

7.1 DATA CHARACTERIZING THE ENVIRONMENT OF MAN-MADE ACCESSES

Chapter 2 and Appendix A present the first attempt at tabulating environmental conditions and factors that influence preconceptual plug design and materials selection. The tabulation, as it now stands, reflects the current knowledge on a large number of conditions and parameters. Many of the values for physical and chemical parameters presented in Table A-I (Appendix A) are based on only a limited number of measurements and/or tests. Design conditions (such as borehole diameters, hydraulic gradients, lithostatic stress, etc.) included on the table are preliminary in nature and are subject to significant future revision.

Thus, the total characterization of man-made accesses and the plug-seat environment will undergo constant review, and any value on Table A-I should be used with these limitations in mind. In addition, Table A-I (though reasonably comprehensive in nature) will need to be enlarged as plugging requirements are improved. Not all possible design conditions, chemical and physical parameters, and other environmental considerations have been listed; more will be identified and will require clarification and data.

7.2 THE MATERIALS SELECTION PROCESS

Chapter 3 and Appendix B present a modified scheme for selecting candidate plug materials. This revised scheme is an outgrowth of earlier materials selection work presented by Taylor and others (1979). The lists of preferred candidate plug materials developed by the present and earlier selection processes are similar; they are by no means considered a final selection of materials for all future plug testing and design. This list is not intended to limit the number of materials that can be considered in plug design and testing programs. The addition of materials that have not yet been considered in selection processes and may have potential application in various plug functions could result in a recasting of the initial, comprehensive list of potential materials. Also, the number of material properties used to rank materials may be expanded, thus requiring modification of the details of the decision analysis discussed in this report.

Another limitation of the materials selection process is that only materials to be used as major plug components were considered; additives (materials added to plugs in small amounts to produce certain desirable conditions) were not included in the screening. However, the testing programs have already begun to rectify this last limitation; various additives (particularly to cements) were investigated as the testing programs proceeded.

7.3 THE MATERIALS TESTING PROGRAMS

The results of the geochemical and physical testing programs described in Chapters 4 and 5 represent the first major steps in further examining and screening candidate plug materials

selected by the process described in Chapter 3. Materials determined suitable for future testing and preconceptual design work as a result of these testing programs will require far more detailed examination before final preconceptual design schemes can be adopted. The results of the materials testing programs are used in preliminary, preconceptual design and for the selection of plug placement equipment. Detailed design work will require advanced geochemical and physical laboratory testing, in-situ borehole testing of plug designs, computer modeling of various plug designs and schemes, and the incorporation of many additional physical and chemical parameters in order to refine the selection of materials, machines, and plug designs. Recommendations presented in the next chapter address future studies that will help overcome limitations discussed in this chapter.

7.3.1 Limitations of the Geochemical Testing Program

Specific limitations on the results of the geochemical testing program relate, in part, to the short time frame under which the program was conducted; 3-month test runs are limited in their ability to completely characterize long-term behavior and reactivities of materials. Also, the shortened time frame did not allow for modifications of experimental procedures as the program progressed. For example, a substitution of gold capsules, after some of the PTFE sample capsules cracked, would have been desirable.

Other limitations on the ability to make more than tentative predictions from these test results relate to how accurately the experiments model the actual physical situation. Bagged powder mixtures in relatively small volumes of static solutions may not be a realistic simulation of the conditions experienced

by a borehole plug material. As discussed in the next chapter, these questions should be considered in the next phase of work.

7.3.2 Limitations of the Physical Testing Program

The most significant limitation of the physical testing was the difficulty of collecting, within a 5-month period, sufficient quantitative experimental data on the short-term and long-term behavior of candidate materials. The scope of the problem is illustrated by the large number of candidate materials and mixtures (28 materials and more than 55 mixtures) and the numerous in-situ hydrological and thermomechanical conditions needed for laboratory simulation. In particular:

- Proportioning data of preferred cement mixtures still need to be refined by taking into consideration the initial in-situ temperature and moisture conditions;
- A relatively moderate expansive behavior was observed for the expansive cement used in the physical testing program, contradicting other project-related test results cited in the literature. Thus, it seems wise to extend the testing to a brand of expansive cement other than Chem Com cement;
- The two months scheduled for permeability tests proved insufficient to allow complete saturation of the miniature, compacted bentonite/sand plugs. Nevertheless, quantitative data on permeability and bond strength of saturated plug samples (cured and tested at low and high temperatures) are still useful in helping to determine the optimum clay content in mixtures and in confirming the suitability of such mixtures for plugging; and

- Model results for premixed clay slurry/aggregate samples are promising but are still preliminary and qualitative. In order to complete a suitability evaluation of plug systems, numerous physical parameters (needed for design) must still be determined. Foremost among these are: (1) the thermal expansion coefficient of preferred plug materials; and (2) the short-term elastoplastic behavior and the long-term visco-elastoplastic behavior of preferred plug materials under simulated in-situ conditions.

8 CONCLUSIONS AND RECOMMENDATIONS

This report describes work recently completed for the BWIP. The following primary objectives of the study (described in Chapter 1 of this report) have been met during this phase of work:

- Man-made accesses to a repository in basalt and details of the plug environment have been characterized. This characterization is in the form of a lengthy tabulation, and known and postulated conditions for these accesses and the environment are referenced (Chapter 2 and Appendix A);
- The materials selection process developed earlier (Taylor and others, 1979) was reviewed and modified. The modified selection process was by decision analysis. The list of preferred candidate materials developed by the modified selection process confirmed the general validity of the list of preferred materials developed earlier;
- Geochemical and physical testing programs for evaluating the chemical stability and physical properties of candidate plug materials were completed (Chapters 4 and 5, and Appendix C); and
- The results of the testing programs were used to evaluate the suitability of materials from the preferred candidate list for use in preliminary preconceptual plug designs (to be described in a separate report).

8.1 CONCLUSIONS

The major conclusions from the work described in this report are:

- The available data on environmental conditions (both natural and man-made) at the Hanford Site are sufficient for preconceptual plug system design. These data are preliminary in nature and will require verification, expansion, and clarification as work on plug system design continues;
- The process for materials selection has been documented by the present work;
- The results of the geochemical testing program indicate that preferred candidate plug materials are chemically non-reactive during laboratory tests that simulated some of the expected environmental conditions;
- On the basis of geochemical test results, all tested materials are considered suitable for consideration in future test programs and in preconceptual plug design. Agitated, crushed-basalt samples and mixtures containing basalt were found to be self-cementing under the hydrothermal conditions of the laboratory tests. This ability is considered a positive finding for this material.
- On the basis of physical test results, those materials considered most suitable for consideration in future test programs and preconceptual plug design are mixtures of natural materials (basalt, clay, glaciofluvial sand,

gravel, and zeolite) and processed natural materials (portland cement Type V and grouts plus additives). Specific proportions and components are discussed in this report; and

- On the basis of results from both geochemical and physical testing programs, those materials considered most suitable for future test programs and preconceptual plug design are combinations of natural and processed natural materials, most of which are readily available at or near the Hanford Site. Most importantly, all of these materials exhibit chemical stability under conditions that partially simulate the expected plug environment, and all can be combined and engineered under laboratory conditions to produce mixtures that have low permeabilities and/or requisite structural strength and other behavioral characteristics desirable in preconceptual plug designs.

8.2 RECOMMENDATIONS

The following recommendations appear appropriate in view of the above results:

- A comprehensive program should be developed for the advanced testing of chemical stability factors critical to the performance of borehole plug materials used in plug systems. This program should include: (1) the elements of an exploratory testing phase that will help determine the experimental procedures for future testing; (2) an approach to the long-term testing and computer modeling of reaction rates (kinetics of reactions) using preferred candidate materials; (3) an approach to

measuring ion exchange potentials and sorption capacities of various borehole plugs designed from preferred materials; (4) an approach to examining the effect of pH on leach rates of plug materials; (5) an approach to examining the deterioration of mechanical properties of plug materials due to chemical reactions; (6) an approach to examining the self-cementing properties of plug materials (particularly basalt) in order to identify the chemical processes involved and ways of promoting these reactions; and (7) a long-term plan for geochemical testing.

- An advanced physical testing program should be developed to support repository backfill and borehole plugging needs during field testing, demonstration, licensing, and construction. This program should include: (1) the development of concepts and a detailed program plan for advanced physical testing; (2) modification and procurement of selected testing equipment and the acquisition of materials for testing; (3) advanced testing that screens some materials at elevated temperature for repository backfill and for canister plug placement (100°C to 400°C), including autoclave curing of candidate materials followed by compression and permeability tests at ambient temperatures projected for the plug environment; (4) the assessment of the coefficient of thermal expansion and, possibly, thermal conductivity of selected plug materials; (5) the assessment of the potential of some soft plug materials to act in a fluid manner; (6) the assessment of creep characteristics of some low temperature plug materials; (7) the determination of bond strengths of monolithic plug-wall rock interfaces after thermal cyclic loading;

(8) the use of a multizone-plug/wall-rock model to quantify the nature of changes in permeability and bond strength due to multizone conditions; and (9) an advanced testing program that identifies rates and selects high-temperature, high-pressure laboratory tests that will model the performance of plug materials and plug systems under simulated in-situ conditions (including temperatures up to 400°C).

- Analytical modeling of borehole plug design and systems should be undertaken to serve several purposes in the design/construction process: (1) preliminary studies would permit the identification of critical parameters/conditions requiring more careful examination in planned field studies; (2) such analyses would provide the basis to predict (forecast) relevant performance patterns and would assist in designing experiments (e.g., instrumentation selection and configuration); (3) experimental evaluations would provide the basis for refining models and analytical techniques and for determining the reliability of existing methods in predicting performance; and (4) optimization of analysis capabilities should be accomplished concurrently with preliminary field test programs in order to effectively meet the design, construction, and monitoring objectives of the program. The approach should be to model some of the key aspects of plug behavior and to coordinate this work with the development of a field test of shallow borehole plugging systems.

- A program should be undertaken to evaluate the impact on the design and performance of borehole plugs of natural fractures in basalt flows and the effects of disturbed rock and rock fracturing that may accompany tunnel and shaft excavations and related repository borings. Specification control and monitoring of the boring or excavation process can help to minimize the man-made disturbance and fractures. The proposed study should include: (1) an evaluation of mechanisms and past field experience in underground excavations; (2) an evaluation of the degree of fracturing that may occur around a borehole, the size of fractures that can be filled, and the effect of structural reinforcement and grout type on long-term plug performance; (3) an evaluation of rock reinforcement techniques (such as spiling or bolting of large diameter excavations) in order to minimize the zone of disturbed rock around the excavation; (4) a review and evaluation of grouting theory, practice, and field results for the sealing of both existing and man-made fractures in hard-rock formations; and (5) laboratory testing designed to support this phase of the work.

- A field test of shallow borehole plugging should be performed at the Hanford Site. This field testing should examine leading candidate plug materials and plug placement schemes and should incorporate data and results from work to date and programs described in the other recommendations above. Initial field testing work should include: (1) a consideration of various options for in-situ mechanical, hydraulic, and geophysical testing; (2) a selection of tests for the separate environments of boreholes (small boreholes, shafts, and tunnels); and

(3) a selection of the various plug options (plugs designed from natural materials, cement plugs, and solid machined plugs) considered appropriate for field testing.

These are the primary recommendations to be made from the results of the present studies. A separate report will present in greater detail a discussion of preconceptual plug systems and placement equipment; that discussion will provide additional data and results that led to some of the above recommendations.

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APPENDIX A

SELECTED PRECONCEPTUAL DESIGN CONDITIONS
OF THE PLUG ENVIRONMENT

APPENDIX A

SELECTED PRECONCEPTUAL DESIGN CONDITIONS
OF THE PLUG ENVIRONMENT

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APPENDIX A
SELECTED PRECONCEPTUAL DESIGN CONDITIONS
OF THE PLUG ENVIRONMENT

INTRODUCTION

This appendix presents a preliminary listing of some assumed preconceptual design conditions (both natural and man-made) of the plug environment at the Hanford Site. Table A-I, which presents this list of conditions, is divided into data on assumed physical conditions and data on assumed chemical conditions. These conditions are tabulated with respect to four possible subsurface micro-environments: boreholes starting at the surface; boreholes starting in the subsurface, tunnels, and shafts. The physical and chemical conditions included in this document are based primarily on published data, on data transmitted from personal communication from Rockwell to WCC, and, to a lesser extent, on subjective judgment. The data base from which many of these conditions and values were obtained is tabulated in Table A-II, and the publications containing the complete data sets are included in the reference list for this appendix.

The design conditions contained in Table A-I are preliminary and tentative. However, they appear reasonable in light of current knowledge and concepts and will be used until alternative or confirmed data become available. In general, the "assumed values" listed in Table A-I under the headings "Boreholes that Start in the Surface" and "Shafts" represent the arithmetic mean obtained from one or more data sets representing a range of depths and variations in material. Where several data sets are available, a weighted mean based on the number of pieces of data is used. The "assumed values"

listed for "Boreholes that Start in the Subsurface" and "Tunnels" are based on data from the Umtanum flow, where such data are available. Data from the Pomona flow, or from the depth range within which the repository is to be located, are given the next order of priority in the absence of data specifically designated as being obtained from the Umtanum flow. Finally, data from Columbia Plateau basalts are given precedence over data obtained from basalt sequences in other regions. Values and discussions in Table A-I for conditions having no supporting laboratory or field data are subjective and judgmental in nature; they should be viewed as preliminary working hypotheses.

This appendix is a working document that may be revised, and the conditions and values presented herein should not be considered final. Some values are based on a relatively limited number of laboratory tests on small samples, which may not be entirely representative of average in-situ conditions encountered during actual excavation of the repository. Chemical data obtained for ground water extracted from depths at which the repository is likely to be located are probably relatively reliable. The least reliable laboratory data are considered to be those obtained for sonic velocities and for permeabilities. Field data on hydraulic gradients (to the extent that they are available) are equivocal. Thus, for a variety of reasons, it is anticipated that some of the assumed values presented herein will be modified or superseded as additional data become available. The emphasis of future data gathering efforts should be on those parameters that have the greatest effect on preconceptual plug designs.

TABLE A-1
PRECONCEPTUAL DESIGN CONDITIONS

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.0 PHYSICAL PARAMETERS				
1.1 <u>Thermal Properties and Conditions</u>				
1.1.1 Specific Heat	<u>Assumed Value</u> 0.319 cal/gm°C at 100°C <u>Range of Values</u> (0.17 cal/gm°C at 38°C) to (0.585 cal/gm°C at 300°C) <u>Comments</u> Varies with temperature. Assumed value is average for Pomona flow.			
1.1.2 Thermal Conductivity	<u>Assumed Value</u> 1.05×10^{-2} W/cm°K <u>Range of Values</u> $(0.654 \text{ to } 1.28) \times 10^{-2}$ W/cm°K <u>Comments</u> 100°C	<u>Assumed Value</u> 1.188×10^{-2} W/cm°K at 100°C <u>Range of Values</u> $(0.799 \text{ to } 1.720) \times 10^{-2}$ W/cm°K at 100°C <u>Comments</u> 1000 to 1470 m	<u>Assumed Value</u> 1.05×10^{-2} W/cm°K <u>Range of Values</u> $(0.654 \text{ to } 1.28) \times 10^{-2}$ W/cm°K <u>Comments</u> 100°C	
1.1.3 Thermal Diffusivity	<u>Assumed Value</u> 0.00511 cm ² /second at 93°C <u>Range of Values</u> (0.00441 to 0.0080 cm ² /second at 316°C) to (0.00532 cm ² /second at 38°C) <u>Comments</u> Varies with temperature.			

A-3

RHO-BWI-C-66

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.1.4 Thermal Expansion Coefficient	Value varies with density; empirical equation of best fit line is: $\alpha = 1.11 + (2.28 \times \rho)$ where α = microstrains per degree centigrade ρ = grams per cc			
1.1.5 Temperature	<u>Assumed Values</u> 42°C <u>Range of Values</u> 15 to 70°C <u>Comments</u> Average from ground surface to Umtanum flow.	<u>Assumed Value</u> 60°C <u>Range of Values</u> 45 to 70°C <u>Comments</u> Umtanum Benson (1978) p. 17 and Fig. 2; p. 3.	<u>Assumed Value</u> 60°C <u>Range of Values</u> 45 to 70°C <u>Comments</u> Umtanum Benson (1978) p. 17 and Fig. 2; p. 3.	<u>Assumed Value</u> 42°C <u>Range of Values</u> 15 to 70°C <u>Comments</u> Average from ground surface to Umtanum flow.
1.1.6 Temperature of Plug and Wall Rock (Operating Conditions)	N. A.	<u>Assumptions</u> Temperature of plug will reach maximum of 100°C, then will cool to about 50°C.		

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.2 <u>Hydraulic Properties and Conditions</u>				
1.2.1 Distance to Nearest Potentially Permeable Zone	<u>Assumed Value</u> 0 m <u>Range of Values</u> 0 to ? <u>Comments</u> Hole may penetrate zone where irrigation water may be collected and returned to the biosphere.	<u>Assumed Value</u> 30 m <u>Range of Values</u> 30 to 50 m <u>Comments</u> Assumes repository flow is 60 to 100 m thick.	<u>Assumed Value</u> 25 m <u>Range of Values</u> 25 to 45 m <u>Comments</u> Assumes repository flow is 60 to 100 m thick.	<u>Assumed Value</u> 0 m <u>Range of Values</u> 0 to ? <u>Comments</u> Shaft may penetrate zone where irrigation water may be collected and returned to the biosphere.
1.2.2 Distance to nearest pumped aquifer	<u>Assumed Value</u> 0 m <u>Range of Values</u> 0 to ? <u>Comments</u> Hole may penetrate Vantage Member.	<u>Assumed Value</u> 250 m <u>Range of Values</u> 250 to 600 m <u>Comments</u> Assumes Vantage Member is nearest pumped aquifer and repository flow is 250 to 600 m below this horizon.	<u>Assumed Value</u> 250 m <u>Range of Values</u> 250 to 600 m <u>Comments</u> Assumes Vantage Member is nearest pumped aquifer and repository flow is 250 to 600 m below this horizon.	<u>Assumed Value</u> 0 m <u>Range of Values</u> 0 to ? <u>Comments</u> Shaft will penetrate Vantage Member.

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.2.3 Distance to Nearest Pumpable Aquifer	<u>Assumed Value</u> 0 m <u>Range of Values</u> 0 to 600 m <u>Comments</u> Assumes hole stops at Vantage Member and that pumpable aquifer may exist at repository flow boundary.	<u>Assumed Value</u> 400 m <u>Range of Values</u> 30 to 600 m <u>Comments</u> Assumes holes are at some distance below the Vantage Member and another lower aquifer.	<u>Assumed Value</u> 375 m <u>Range of Values</u> 25 to 600 m <u>Comments</u> Assumes holes are at some distance below the Vantage Member and another lower aquifer.	<u>Assumed Value</u> 0 m <u>Range of Values</u> 0 to ? m <u>Comments</u> Assumes access shafts will penetrate all potential aquifers.
1.2.4 Hydraulic Conductivity (Permeability Coefficient)	<u>Assumed Value</u> 10^{-9} cm/sec <u>Range of Values</u> 10^{-3} to 10^{-13} cm/sec <u>Comments</u> High values in flow tops.			
1.2.5 Transmissivity	<u>Assumed Value</u> $0.20 \text{ m}^2/\text{day}$ <u>Range of Values</u> (1.6×10^{-3}) to $7.2 \text{ m}^2/\text{day}$			
1.2.6 Apparent Porosity	<u>Assumed Value</u> 1.24% <u>Range of Values</u> 1.0 to 2.4% <u>Comments</u> Pomona flow.			

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.2.7 Hydraulic Gradient (Horizontal) (Pre-mining)		<u>Assumed Value</u> 1×10^{-4} <u>Range of Values</u> (5×10^{-5}) to (5×10^{-4}) <u>Comments</u> Deju and others (1978), Table I, p. 9.		
1.2.8 Hydraulic Gradient (Vertical) (Pre-mining)		<u>Assumed Value</u> 1×10^{-3} <u>Range of Values</u> (5×10^{-4}) to (4×10^{-1}) <u>Comments</u> Deju and others (1978), Table I, p. 9.		
1.2.9 Long-Term Hydraulic Gradients (with thermal influence)		<u>Assumed Value</u> 1 m/km horizontal and 1 m/100 m upward <u>Unknown</u> Steady state flow conditions (expanding thermal effects)		

TABLE A-1 (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.2.10 Rewatering	N. A.	N. A.	<p><u>Assumptions</u> Natural rewatering takes 10 years to fill repository. Maximum differential hydraulic head to be studied is 1,000 m on plug pushing <u>in</u> toward repository due to shaft or borehole filling with water while repository is dry. Maximum differential hydraulic head to be studied is 160 m on plug pushing <u>out</u> due to heating of water and steam in repository.</p> <p><u>Unknowns</u> Natural or accelerated? How long will rewatering take? Will plug dry out? How long will repository be exposed to steam? What is the worst differential head on plug during rewatering?</p> <p><u>Comments</u> The actual time required to rewater the excavation will be a function of both permeability of the wall rock and the void space left in the backfill.</p>	
1.2.11 Hydrostatic Head	<p><u>Assumed Value, MPa</u> $10^{-2} z$, where z = depth (in meters)</p> <p><u>Range of Values</u> 0 to 15 MPa</p>	<p><u>Assumed Value, MPa</u> $10^{-2} z$, where z = depth (in meters)</p> <p><u>Range of Values</u> 10 to 15 MPa</p>	<p><u>Assumed Value, MPa</u> $10^{-2} z$, where z = depth (in meters)</p> <p><u>Range of Values</u> 10 to 15 MPa</p>	<p><u>Assumed Value, MPa</u> $10^{-2} z$, where z = depth (in meters)</p> <p><u>Range of Values</u> 0 to 15 MPa</p>
1.2.12 Moisture Conditions of Holes at Plug Seat	<p><u>Assumed Value</u> Wet</p> <p><u>Range of Values</u> None</p> <p><u>Comments</u> Assume that plugs will be placed in wet boreholes.</p>		<p><u>Assumed Value</u> Dry</p> <p><u>Range of Values</u> Dry to Wet</p> <p><u>Comments</u> Maintained dry for plug placement.</p>	

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.3 <u>Mechanical Properties and Conditions</u>				
1.3.1 Thickness of Repository Flow	N. A.	<u>Assumed Value</u> 60 m <u>Range of Values</u> 60 to 100 m		N. A.
1.3.2 Fracture Spacing	<u>Assumed Value</u> 10 per meter <u>Range of Values</u> 1 to 28 per meter <u>Comments</u> Well DH-5 Long (1978)			
1.3.3 Casings/Linings of Plug Seats	<u>Assumed Value</u> Uncased <u>Range of Values</u> Casing <u>Comments</u> Assumes casing will be removed prior to plugging.	<u>Assumed Value</u> Uncased <u>Range of Values</u> Uncased or filled with grout or steel <u>Comments</u> Assumes open holes will be uncased.	<u>Assumed Value</u> Unlined <u>Range of Values</u> Unlined to lined with shotcrete, gunite, concrete, etc.	<u>Assumed Value</u> Lined <u>Range of Values</u> Unlined to lined <u>Comments</u> Assumes lining may be removed prior to plugging.
1.3.4 Radius of Induced Fracturing Around Hole	<u>Assumed Value</u> No fracturing	<u>Assumed Value</u> No fracturing	Data Needed	Data Needed

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.3.5 Wall Rock Type at Plug Seat	<u>Assumed Value</u> Basalt and basalt interflow material <u>Range of Values</u> Basalt, flow tops, and sedimentary units <u>Comments</u> Hole intersects various rock types.	<u>Assumed Value</u> Basalt <u>Range of Values</u> None <u>Comments</u> Hole is within repository flow.	<u>Assumed Value</u> Basalt <u>Range of Values</u> None <u>Comments</u> Hole is within repository flow.	<u>Assumed Value</u> Basalt and basalt interflow material <u>Range of Values</u> Basalt, flow tops, and sedimentary units <u>Comments</u> Hole intersects various rock types.
1.3.6 Hole Diameter at Repository Depth	<u>Assumed Value</u> 17 cm (6-3/4 inches) <u>Range of Values</u> 5 to 25 cm <u>Comments</u> Holes smaller than 10 cm will probably be re-drilled to a larger diameter.	<u>Assumed Value</u> 10 cm <u>Range of Values</u> 7 to 14 cm	<u>Assumed Value</u> 7 m <u>Range of Values</u> 6 to 10 cm	<u>Assumed Value</u> 6 m <u>Range of Values</u> 2 to 9 m
1.3.7 Hole Depth-Length	<u>Assumed Value</u> 1,000 m <u>Range of Values</u> 900 to 1,500 m <u>Comments</u> Assumes repository depth in excess of 900 m.	<u>Assumed Value</u> 15 m <u>Range of Values</u> 5 to 50 m <u>Comments</u> Assumes holes will be exploratory or for advancing tunnels.	<u>Assumed Value</u> 3 km <u>Range of Values</u> 3 to 8 km <u>Comments</u> Assumes tunnels will be approximately 3 km long.	<u>Assumed Value</u> 1,000 m <u>Range of Values</u> 900 to 1,500 m <u>Comments</u> Assumes repository depth to exceed 900 m.

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.3.8 Lithostatic Pressure (Horizontal) (Cook, 1977)	<u>Assumed Maximum Stress (for $z > 100$ m)</u> $27.3 + 0.0218 z$ where z = depth (in meters) <u>Range of Values</u> $(23.5 + 0.0188 z)$ to $(30.4 + 0.0243 z)$ <u>Assumed Minimum Stress (for $z > 100$ m)</u> $2.73 + 0.011 z$ <u>Range of Values</u> $(2.35 + 0.0094 z)$ to $(3.04 + 0.0122 z)$		<u>Assumed Maximum Stress</u> 49 MPa <u>Range of Values</u> 42 to 55 MPa @ 1,000 m <u>Assumed Minimum Stress</u> 14 MPa <u>Range of Values</u> 12 to 15 MPa @ 1,000 m	<u>Comments</u> See data at left for "boreholes."
1.3.9 Lithostatic Pressure (Vertical)	<u>Assumed Value</u> 21 MPa <u>Range of Values</u> 0 to 42 MPa <u>Comments</u> Average vertical stress from surface to repository depth.	<u>Assumed Value</u> 35 MPa <u>Range of Values</u> 28 to 42 MPa <u>Comments</u> Vertical stress between 1,000 and 1,500 m	<u>Assumed Value</u> 35 MPa <u>Range of Values</u> 28 to 42 MPa <u>Comments</u> Vertical stress between 1,000 and 1,500 m. Benson (1978) calculated a pressure of 270 bars.	<u>Assumed Value</u> 21 MPa <u>Range of Values</u> 0 to 42 MPa <u>Comments</u> Average vertical stress from surface to repository depth.
1.3.10 Angle of Internal Friction	<u>Assumed Value</u> 46 degrees <u>Range of Values</u> 28 to 58 degrees <u>Comments</u> Colorado School of Mines (1978)			

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TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.3.11 Cohesion	<u>Assumed Value</u> 32 MPa <u>Range of Values</u> 15 to 38 MPa <u>Comments</u> Value for basalt.			
1.3.12 Density (Bulk)	<u>Assumed Value</u> 2.72 gm/cc <u>Range of Values</u> 1.75 to 2.88 gm/cc <u>Comments</u> DC-11; DH-2,3,4,5	<u>Assumed Value</u> 2.79 gm/cc <u>Range of Values</u> 2.67 to 2.85 gm/cc <u>Comments</u> DH-3,4,5; 1,009 to 1,475 m		<u>Assumed Value</u> 2.72 gm/cc <u>Range of Values</u> 1.75 to 2.88 gm/cc <u>Comments</u> DC-11; DH-2,3,4,5
1.3.13 Density (Grain)	<u>Assumed Value</u> 2.87 gm/cc <u>Range of Values</u> 2.4 to 3.1 gm/cc			
1.3.14 Poisson's Ratio	<u>Assumed Value</u> 0.249 <u>Range of Values</u> 0.115 to 0.513 <u>Comments</u> 81 Triax tests, various depths; Colorado School of Mines (1978)	<u>Assumed Value</u> 0.259 <u>Range of Values</u> 0.142 to 0.513 <u>Comments</u> 36 Triax tests, 1,035 to 1,470 m, Colorado School of Mines (1978)		<u>Assumed Value</u> 0.249 <u>Range of Values</u> 0.115 to 0.513 <u>Comments</u> 81 Triax tests, various depths; Colorado School of Mines (1978)

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TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.3.15 Rigidity Modulus		<u>Assumed Value</u> 33.5 GPa <u>Range of Values</u> 28.4 to 41.6 GPa <u>Comments</u> Axial values from dynamic tests.		
1.3.16 Rupture Modulus		<u>Assumed Value</u> 24 MPa <u>Range of Values</u> 2.4 to 47.8 MPa <u>Comments</u> Pomona flow.		
1.3.17 Tensile Strength		<u>Assumed Value</u> 21 MPa <u>Range of Values</u> 15 to 28.5 MPa <u>Assumed Value</u> Pomona flow		
1.3.18 Triaxial Compressive Strength		<u>Comments</u> See 1.3.10 and 1.3.11 for data to plot strength envelope.		

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TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
1.3.19 Uniaxial Compressive Strength	<u>Assumed Value</u> 218 MPa <u>Range of Values</u> 4 to 378 MPa <u>Comments</u> DC-11; DH-2,3,4,5; Colorado School of Mines (1978)	<u>Assumed Value</u> 219 MPa <u>Range of Values</u> 86 to 378 MPa <u>Comments</u> DH-3,4,5; 1035 to 1470 m; Colorado School of Mines (1978)		<u>Assumed Value</u> 218 MPa <u>Range of Values</u> 4 to 378 MPa <u>Comments</u> DC-11; DH-2,3,4,5; Colorado School of Mines (1978)
1.3.20 Young's Modulus (Dynamic)	<u>Assumed Value</u> 54.2 GPa <u>Range of Values</u> 0.38 to 165 GPa <u>Comments</u> Various depths	<u>Assumed Value</u> 51 GPa <u>Range of Values</u> 2.65 to 142 GPa <u>Comments</u> 1,000 to 1,470 m		<u>Assumed Value</u> 54.2 GPa <u>Range of Values</u> 0.38 to 165 GPa <u>Comments</u> Various depths
1.3.21 Young's Modulus (Static)	<u>Assumed Value</u> 65.4 GPa <u>Range of Values</u> 27.4 to 121.6 GPa <u>Comments</u> Triax tests, 1,035 to 1,470 m.			

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
2.0 GEOCHEMICAL CONDITIONS				
2.1 <u>Ground-water</u> <u>Chemistry</u>				
2.1.1 Bicarbonate	<u>Assumed Value</u> 90 mg/l <u>Range of Values</u> 2 to 315 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 23 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 23 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 90 mg/l <u>Range of Values</u> 2 to 315 mg/l <u>Comments</u> Average
2.1.2 Boron	<u>Assumed Value</u> 0.38 mg/l <u>Range of Values</u> 0 to 0.94 mg/l <u>Comments</u> Average; LaSala and Doty (1971).	<u>Assumed Value</u> 0.17 mg/l <u>Range of Values</u> single sample <u>Comments</u> ARH-DC-1, 978 to 990 m, LaSala and Doty (1971).	<u>Assumed Value</u> 0.17 mg/liter <u>Range of Values</u> single sample <u>Comments</u> ARH-DC-1, 978 to 990 m; LaSala and Doty (1971).	<u>Assumed Value</u> 0.38 mg/l <u>Range of Values</u> 0 to 0.94 mg/l <u>Comments</u> Average; LaSala and Doty (1971).
2.1.3 Calcium	<u>Assumed Value</u> 10.8 mg/l <u>Range of Values</u> 0.5 to 72 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 1.3 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 1.3 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 10.8 mg/l <u>Range of Values</u> 0.5 to 72 mg/l <u>Comments</u> Average

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
2.1.4 Carbonate	<u>Assumed Value</u> 35 mg/l <u>Range of Values</u> 0 to 125 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 17.3 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 17.3 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 35 mg/l <u>Range of Values</u> 0 to 125 mg/l <u>Comments</u> Average
2.1.5 Chloride	<u>Assumed Value</u> 64 mg/l <u>Range of Values</u> 3 to 148 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 148 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 148 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 64 mg/l <u>Range of Values</u> 3 to 148 mg/l <u>Comments</u> Average
2.1.6 Fluoride	<u>Assumed Value</u> 29.5 mg/l <u>Range of Values</u> 20 to 41 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 39 mg/l <u>Range of Values</u> 37 to 41 mg/l <u>Comments</u> Umtanum	<u>Assumed Value</u> 39 mg/l <u>Range of Values</u> 37 to 41 mg/l <u>Comments</u> Umtanum	<u>Assumed Value</u> 29.5 mg/l <u>Range of Values</u> 20 to 41 mg/l <u>Comments</u> Average
2.1.7 Hardness, Total	<u>Assumed Value</u> 56 mg/l <u>Range of Values</u> 1 to 220 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 35 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 35 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 56 mg/l <u>Range of Values</u> 1 to 220 mg/l <u>Comments</u> Average

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
2.1.8 Iron	<u>Assumed Value</u> 0.47 mg/l <u>Range of Values</u> 0 to 2.1 mg/l <u>Comments</u> ARH-DC-1, Average	<u>Assumed Value</u> 0.65 mg/l <u>Range of Values</u> single sample <u>Comments</u> ARH-DC-1, 978 to 990 m	<u>Assumed Value</u> 0.65 mg/l <u>Range of Values</u> single sample <u>Comments</u> ARH-DC-1, 978 to 990 m	<u>Assumed Value</u> 0.47 mg/l <u>Range of Values</u> 0 to 2.1 mg/l <u>Comments</u> ARH-DC-1, Average
2.1.9 Magnesium	<u>Assumed Value</u> 3 mg/l <u>Range of Values</u> 0 to 14 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 0.1 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 0.1 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 3 mg/l <u>Range of Values</u> 0 to 14 mg/l <u>Comments</u> Average
2.1.10 Nitrate	<u>Assumed Value</u> 0.2 mg/l <u>Range of Values</u> 0 to 0.5 mg/l <u>Comments</u> ARH-DC-1, Average	<u>Assumed Value</u> 0.2 mg/l <u>Range of Values</u> single sample <u>Comments</u> ARH-DC-1, 978 to 990 m	<u>Assumed Value</u> 0.2 mg/l <u>Range of Values</u> single sample <u>Comments</u> ARH-DC-1, 978 to 990 m	<u>Assumed Value</u> 0.2 mg/l <u>Range of Values</u> 0 to 0.5 mg/l <u>Comments</u> ARH-DC-1, Average
2.1.11 pH	<u>Assumed Value</u> 8.8 <u>Range of Values</u> 7.3 to 10 <u>Comments</u> Average	<u>Assumed Value</u> 10 <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 10 <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 8.8 <u>Range of Values</u> 7.3 to 10 <u>Comments</u> Average

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
2.1.12 Phosphate	<u>Assumed Value</u> 0.08 mg/l <u>Range of Values</u> 0.01 to 0.25 mg/l <u>Comments</u> ARRH-DC-1, Average	<u>Assumed Value</u> 0.02 mg/l <u>Range of Values</u> single sample <u>Comments</u> ARRH-DC-1, 978 to 990 m	<u>Assumed Value</u> 0.02 mg/l <u>Range of Values</u> single sample <u>Comments</u> ARRH-DC-1, 978 to 990 m	<u>Assumed Value</u> 0.08 mg/l <u>Range of Values</u> 0.01 to 0.25 mg/l <u>Comments</u> ARRH-DC-1, Average
2.1.13 Potassium	<u>Assumed Value</u> 11 mg/l <u>Range of Values</u> 3 to 15 mg/l <u>Comments</u> 110 to 684 m	<u>Assumed Value</u> 5.9 mg/l <u>Range of Values</u> single sample <u>Comments</u> 978 to 990 m	<u>Assumed Value</u> 5.9 mg/l <u>Range of Values</u> single sample <u>Comments</u> 978 to 990 m	<u>Assumed Value</u> 11 mg/l <u>Range of Values</u> 3 to 15 mg/l <u>Comments</u> 110 to 684 m
2.1.14 Silica	<u>Assumed Value</u> 53 mg/l <u>Range of Values</u> 22.5 to 105 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 53.8 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 53.8 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 53 mg/l <u>Range of Values</u> 22.5 to 105 mg/l <u>Comments</u> Average
2.1.15 Sodium	<u>Assumed Value</u> 99 mg/l <u>Range of Values</u> 29 to 242 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 242 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 242 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 99 mg/l <u>Range of Values</u> 29 to 242 mg/l <u>Comments</u> Average

TABLE A-I (continued)

PRE-CONCEPTUAL DESIGN CONDITIONS	BOREHOLES THAT START AT THE SURFACE	BOREHOLES THAT START IN THE SUBSURFACE	TUNNELS	SHAFTS
2.1.16 Sulfate	<u>Assumed Value</u> 30 mg/l <u>Range of Values</u> 0 to 150 mg/l <u>Comments</u> Average	<u>Assumed Value</u> 96 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 96 mg/l <u>Range of Values</u> single sample <u>Comments</u> Umtanum	<u>Assumed Value</u> 30 mg/l <u>Range of Values</u> 0 to 150 mg/l <u>Comments</u> Average
2.1.17 Eh	Assumed to be reducing at plug seats below the water table. The presence of iron pyrite as a stable secondary mineral phase suggests an Eh range of -0.2 to -0.3 volts (Garrels and Christ, 1965). Other secondary minerals present at projected repository depths are also stable in this Eh range and at the assumed pH of approximately 10 (see 2.1.11, above). Both tunnels and shafts will have an oxidizing environment during repository operations prior to plug and backfill placement.			
2.2 <u>Secondary Minerals</u>	<u>Reported Minerals</u> Clinoptilolite Nontronite Cristobalite Quartz Calcite Gypsum Potassium Feldspar Mordenite Pyrite Apatite Opal <u>Comments</u> Benson (1978), page 16			

TABLE A-II
PHYSICAL DATA COMPILATION

PARAMETER	AVERAGE VALUE	RANGE OF VALUES	UNITS	NO. OF TESTS	REMARKS	DATA SOURCE AUTHOR (YEAR)	TABLE	PAGE
THERMAL PROPERTIES								
Specific Heat	0.319	0.288 to 0.355	cal/gm °C	3	Cp 100°C Pomona flow	Duvall and others (1978)	XII	
	0.425	0.394 to 0.460	cal/gm °C	3	Cp 200°C Pomona flow	Duvall and others (1978)	XII	
	0.538	0.474 to 0.585	cal/gm °C	3	Cp 300°C Pomona flow	Duvall and others (1978)	XII	
	0.35	0.23 to 0.25	cal/gm °C	7	"Average" is Columbia Plateau; range is for "average" basalt.	Board (1978)	II	
	0.175	0.174 to 0.176	cal/gm °C	2	37.8°C	ARHCO (1976)	I	120
	0.186	0.186 to 0.187	cal/gm °C	2	93.3°C	ARHCO (1976)	I	120
	0.197	0.197 to 0.198	cal/gm °C	2	149°C	ARHCO (1976)	I	120
	0.208	0.207 to 0.210	cal/gm °C	2	204°C	ARHCO (1976)	I	120
	0.219	0.217 to 0.222	cal/gm °C	2	260°C	ARHCO (1976)	I	120
	0.230	0.227 to 0.234	cal/gm °C	2	316°C	ARHCO (1976)	I	120
	1.0	0.95 to 1.05	kJ/kg °K			Agapito and others (1977)	I	
Thermal Conductivity	0.349	0.310 to 0.384	cal/sec m°C	3	K150°C	Duvall and others (1978)	XI	
	0.347	0.308 to 0.383	cal/sec m°C	3	K200°C	Duvall and others (1978)	XI	
	0.348	0.303 to 0.383	cal/sec m°C	3	K250°C	Duvall and others (1978)	XI	
	0.36	0.335 to 1.0	cal/sec m°C	7	Cites Duvall and others (1978)	Board (1978)	II	
	0.258	0.243 to 0.272	cal/sec m°C	2	37.8°C	ARHCO (1976)	I	120
	0.267	0.249 to 0.284	cal/sec m°C	2	93.3°C	ARHCO (1976)	I	120
	0.275	0.255 to 0.295	cal/sec m°C	2	149°C	ARHCO (1976)	I	120
	0.283	0.260 to 0.305	cal/sec m°C	2	204°C	ARHCO (1976)	I	120
	0.290	0.264 to 0.315	cal/sec m°C	2	260°C	ARHCO (1976)	I	120
	0.300	0.267 to 0.324	cal/sec m°C	2	316°C	ARHCO (1976)	I	120
	1.5	1.4 to 2.8	w/m °K	7	373°K	Agapito and others (1977)	I	
	1.53		w/m °K	7		Agapito and others (1977)	IV	
	1.05×10^{-2}	$(0.654 \text{ to } 1.28) \times 10^{-2}$	w/cm °K	29	All samples, 100°C	Colorado Sch. Mines (1978)	Fig. 15	70
	1.48×10^{-2}	$(0.744 \text{ to } 2.256) \times 10^{-2}$	w/cm °K	29	All samples, 200°C	Colorado Sch. Mines (1978)	Fig. 15	70
	1.9×10^{-2}	$(0.783 \text{ to } 2.992) \times 10^{-2}$	w/cm °K	29	All samples, 300°C	Colorado Sch. Mines (1978)	Fig. 15	70
Thermal Diffusivity	1.188×10^{-2}	$(0.799 \text{ to } 1.720) \times 10^{-2}$	w/cm °K	13	1,005 to 1,470 m, 100°C	Colorado Sch. Mines (1978)		71-74
	1.574×10^{-2}	$(1.047 \text{ to } 1.787) \times 10^{-2}$	w/cm °K	13	1,005 to 1,470 m, 200°C	Colorado Sch. Mines (1978)		71-74
	2.01×10^{-2}	$(1.252 \text{ to } 2.992) \times 10^{-2}$	w/cm °K	13	1,005 to 1,470 m, 300°C	Colorado Sch. Mines (1978)		71-74
	0.00524	0.00516 to 0.00532	cm ² /sec	2	37.8°C	ARHCO (1976)	I	120
	0.00511	0.00503 to 0.00519	cm ² /sec	2	93.3°C	ARHCO (1976)	I	120
	0.00497	0.00488 to 0.00506	cm ² /sec	2	149°C	ARHCO (1976)	I	120
	0.00482	0.00472 to 0.00493	cm ² /sec	2	204°C	ARHCO (1976)	I	120
Thermal Expansion Coefficient	0.00459	0.00457 to 0.00480	cm ² /sec	2	260°C	ARHCO (1976)	I	120
	0.00454	0.00441 to 0.00467	cm ² /sec	2	316°C	ARHCO (1976)	I	120
	0.00650	0.0052 to 0.0080	cm ² /sec	2		Agapito and others (1977)	I	
Thermal Expansion Coefficient	6.5×10^{-6}	$(6.5 \text{ to } 6.7) \times 10^{-6}$	/°C	3	Pomona flow, Gable Mtn.	Duvall and others (1978)	X	
	6.6×10^{-6}	$(2.9 \text{ to } 11.6) \times 10^{-6}$	/°C	7	Columbia Plateau vs. "average"	Board (1978)	II	
	5.4×10^{-6}	$(2.9 \text{ to } 11.6) \times 10^{-6}$	/°K	7	300°K	Agapito and others (1977)	I	
	5.4×10^{-6}	$(4.3 \text{ to } 6.5) \times 10^{-6}$	/°K	7	Empirical equation of best fit line $\alpha = 1.11 + (2.28 \times \rho)$ where α = micro-strains per degree centigrade; ρ = grams per cc.	Agapito and others (1977) Colorado Sch. Mines (1978)	V	66

TABLE A-II (continued)

PARAMETER	AVERAGE VALUE	RANGE OF VALUES	UNITS	NO. OF TESTS	REMARKS	DATA SOURCE AUTHOR (YEAR)	TABLE	PAGE
HYDRAULIC PROPERTIES								
Apparent Porosity	1.89%	1.60 to 2.39%	percent	3	Small samples - Pomona flow	Duvall and others (1978)	IX	
	1.24%	1.00 to 1.59%	percent	3	Large samples - Pomona flow	Duvall and others (1978)	IX	
Hydraulic Conductivity	10 ⁻¹⁰	10 ⁻⁷ to 10 ⁻¹³	cm/sec	?	Preliminary data	Biggerstaff (1978)		109
	10 ⁻¹⁰	10 ⁻³ to 10 ⁻¹³	m/sec	14	Vesicular and rubbly flow tops	Gephart and others (1978)	1	
	10 ⁻⁶	10 ⁻⁶ to 10 ⁻⁷	cm/sec	3	Papadopoulos method	Science App. (1978)	2	11
	10 ⁻⁸	10 ⁻⁶ to 10 ⁻⁸	cm/sec	3	USBR method	Science App. (1978)	2	11
	10 ⁻¹⁰	10 ⁻⁹ to 10 ⁻¹²	cm/sec	6	Hvorslev method	Science App. (1978)	2	11
Transmissivity	21.6	0.17 to 77.9	ft ² /day	18		LaSala and Doty (1971)	4	24
MECHANICAL PROPERTIES								
Angle of Internal Friction	55°	45° to 60°	degrees	?	Summarized from Agapito and others (1977)?	Boaid (1978)	II	
	55°	45° to 60°	degrees			Agapito and others (1977)	I	
	52°	42° to 59°	degrees	6		Agapito and others (1977)	XIII	
Bulk Modulus	(42.0) (35.5) x 10 ³	(26.1 to 54.7) (44.8 to 41.2) x 10 ³	MPa	19	Axial/Diametral Pomona flow	Duvall and others (1978)	VII	
Cohesion	32	15 to 38	MPa	6		Agapito and others (1977)	XIII	
Density (Bulk)	2.83	2.78 to 2.87		9	Pomona flow, Gable Mtn.	Duvall and others (1978)	I	
	2.81	2.78 to 2.84		3	Pomona flow, Gable Mtn.	Duvall and others (1978)	VIII	
	2.80	2.66 to 2.94		2	37.8°C; depth 306 to 330 m	ARHCO (1976)	I	120
	2.80	2.66 to 2.94		2	93.3°C	ARHCO (1976)	I	120
	2.81	2.65 to 2.95		2	149°C	ARHCO (1976)	I	120
	2.81	2.67 to 2.95		2	204°C	ARHCO (1976)	I	120
	2.81	2.67 to 2.95		2	260°C	ARHCO (1976)	I	120
	2.81	2.67 to 2.95		2	316°C	ARHCO (1976)	I	120
	2.9	2.40 to 3.10		?		Agapito and others (1977)	I	
	2.70	2.46 to 2.90		14		Agapito and others (1977)	XI	
	2.79	2.67 to 2.85	gm/cc	26	DH-3,4,5; 1,005 to 1,470 m	Colorado Sch. Mines (1978)		7-9
	2.72	1.75 to 2.88	gm/cc	84	DC-11, DH-2,3,4,5; all samples	Colorado Sch. Mines (1978)		7-9
Density (Grain)	2.87	2.85 to 2.89		3	Pomona flow, Gable Mtn	Duvall and others (1978)	VIII	
	2.87	2.4 to 3.1		?	Cites Duval and others (1978)	Board (1978)	II	

TABLE A-II (continued)

PARAMETER	AVERAGE VALUE	RANGE OF VALUES	UNITS	NO. OF TESTS	REMARKS	DATA SOURCE AUTHOR (YEAR)	TABLE	PAGE
Dynamic Wave Velocities	5599 5717	5242 to 5991 5277 to 5937	ft/sec	18	Axial/diametral vs. Pomona flow, Gable Mtn	Duvall and others (1976)	VI	
	3480 3832	3193 to 3819 3958 to 3653	ft/sec	18	Axial/diametral vs Pomona flow, Gable Mtn.	Duvall and others (1976)	VI	
Lame's Constant	19.7 9.0	-1.6 to 32.4 24.4 to 11.1	MPa	19	Axial/diametral Pomona flow	Duvall and others (1978)	VII	
Poisson's Ratio (Dynamic)	0.183 0.069	-0.021 to 0.229 0.195 to 0.10		19	Axial/diametral Pomona flow	Duvall and others (1978)	VII	
Poisson's Ratio (Static)	0.25	0.191 to 0.290		9	Uniaxial tests, Pomona flow	Duvall and others (1978)	V	37-39 40-42 37-39 40-42
	0.25	0.215 to 0.286		9	Triaxial tests; Pomona flow	Duvall and others (1978)	V	
	0.26	0.22 to 0.28		?	Bacon Siphon, Columbia Basin	Agapito and others (1977)	I	
	0.17	0.05 to 0.31		12		Agapito and others (1977)	XI	
	0.249	0.115 to 0.513		81	Triax - all samples	Colorado Sch. Mines		
	0.259	0.130 to 0.554		84	Uniax - all samples	Colorado Sch. Mines		
	0.259	0.142 to 0.513		36	Triax - 1034 to 1470 m	Colorado Sch. Mines		
	0.254	0.130 to 0.554		41	Uniax - 1034 to 1470 m	Colorado Sch. Mines		
Rigidity Modulus (Dynamic)	$(\frac{33.5}{40.5}) \times 10^3$	$(\frac{28.4}{43.6} \text{ to } \frac{41.6}{28.1}) \times 10^3$	MPa	19	Axial/diametral Pomona flow	Duvall and others (1978)	VII	
Rupture Modulus	24	2.42 to 47.8	MPa	12	Pomona flow, Gable Mtn.	Duvall and others (1978)	IV	
Tensile Strength	21	15 to 28.5	MPa	9	Pomona flow, Gable Mtn.	Duvall and others (1978)	II	48
	21	0 to 23	MPa	?		Board (1978)	II	
	14	0 to 23	MPa	?		Agapito and others (1977)	I	
	18.4	2.8 to 33.9	MPa	6		LaSala and Doty (1971)	VI	
Triaxial Compressive Strength	273	141 to 379	MPa	9	Pomona flow, Gable Mtn. Various confining pressures	Duvall and others (1978)	III	
	290	16 to 638	MPa	59		Agapito and others (1977)	XII	
Uniaxial Compressive Strength	309	248 to 378	MPa	9	Pomona flow, Gable Mtn. DH-4, 1177 to 1364 m DH-5, 1006 to 1470 m DH-3, 1034 to 1069 m DC-11, DH-2,3,4,5, all samples	Duvall and others (1978)	I	48 7 8 9 7-9
	284	0 to 400	MPa	?		Board (1978)	II	
	200	0 to 400	MPa	?		Agapito and others (1977)	I	
	159	74 to 322	MPa	6		LaSala and Doty (1971)	6	
	195.3	84.3 to 287.9	MPa	9		Colorado Sch. Mines (1978)		
	247.3	85.6 to 378.2	MPa	9		Colorado Sch. Mines (1978)		
	210.4	160.6 to 304.9	MPa	5		Colorado Sch. Mines (1978)		
	218	4 to 378	MPa	84		Colorado Sch. Mines (1978)		

TABLE A-II (continued)

PARAMETER	AVERAGE VALUE	RANGE OF VALUES	UNITS	NO. OF TESTS	REMARKS	DATA SOURCE AUTHOR (YEAR)	TABLE	PAGE
Young's Modulus (static)	76	64 to 87	GPa	9	Uniaxial tests, Pomona flow	Duvall and others (1978)	V	
	77	63.1 to 85.5	GPa	9	Triaxial tests, Pomona flow	Duvall and others (1978)	V	
	77	61 to 112	GPa	?		Board (1978)	II	
	111.5	111.5	GPa	1	Basalt. Ostritz, Germany	Agapito and others (1977)	VI	
	61	61	GPa	1	Basalt. Michigan	Agapito and others (1977)	VI	
	85	85	GPa	1	Basalt. Michigan	Agapito and others (1977)	VI	
	88.5	88.5	GPa	1	Basalt. Wisconsin	Agapito and others (1977)	VI	
	60	45 to 80	GPa	12	Bacon Siphon-Columbia Basin	Agapito and others (1977)	XI	
	6.54×10^4	$(2.74 \text{ to } 12.16) \times 10^4$	MPa	36	Triax, 1,034 to 1,470 m	Colorado Sch. Mines (1978)		37-39
	5.78×10^4	$(1.39 \text{ to } 9.45) \times 10^4$	MPa	42	Uniax, 1,006 to 1,470 m	Colorado Sch. Mines (1978)		40-42
	6.52×10^4	$(1.32 \text{ to } 12.16) \times 10^4$	MPa	81	Triax, all samples	Colorado Sch. Mines (1978)		37-39
	6.01×10^4	$(0.77 \text{ to } 9.45) \times 10^4$	MPa	84	Uniax, all samples	Colorado Sch. Mines (1978)		40-42
Young's Modulus (Dynamic)	$(72.7 \text{ to } 75.3) \times 10^3$	$(69.8 \text{ to } 89.8) \times 10^3$	GPa	19	Uniaxial tests, Pomona flow	Duvall and others (1978)	VII	
	5.42×10^4	$(0.038 \text{ to } 16.5) \times 10^4$	MPa	214	Lab, all samples	Colorado Sch. Mines (1978)		55-60
	5.10×10^4	$(0.265 \text{ to } 14.2) \times 10^4$	MPa	110	Lab, 1,006 to 1,470 m	Colorado Sch. Mines (1978)		55-60

TABLE A-II (continued)

PARAMETERS	AVERAGE VALUE*	RANGE OF VALUES*	REMARKS	DATA SOURCE AUTHOR (YEAR)	DATA SOURCE TABLE / PAGE	
Bicarbonate	172	115 to 315	Unconfined aquifer	ARHCO (1976)	III	18
	152	93 to 180	Uppermost confined aquifer	ARHCO (1976)		
	56	2 to 164	Lower confined aquifers	ARHCO (1976)		
	42.8		Grande Ronde Basalt (RSH-1)	Deju (1978)		
	180		Mabton Member	Deju (1978)	Fig. 5	18
	23		Umtanum basalt	LaSala and Doty (1971)	7	50
	2		ARH-DC-1, 978 to 990 m			
Boron	0.17		ARH-DC-1; 978 to 990 m	LaSala and Doty (1971)	7	50
Calcium	48	31 to 72	Unconfined aquifer	ARHCO (1976)	III	18
	15	1 to 18	Uppermost confined aquifer	ARHCO (1976)		
	0.5	0.2 to 0.8	Lower confined aquifer	ARHCO (1976)		
	6.5		Grande Ronde Basalt (RSH-1)	Deju (1978)		
	3.4		Mabton Member	Deju (1978)	Fig. 5	18
	1.3		Umtanum basalt	LaSala and Doty (1971)	7	50
	0.6		Umtanum Basalt (DC-6)			
<p>*All values, except pH, are in mg/l</p>						

TABLE A-II (continued)

PARAMETERS	AVERAGE VALUE*	RANGE OF VALUES*	REMARKS	DATA SOURCE AUTHOR (YEAR)	DATA SOURCE TABLE / PAGE	
Carbonate	0 3 87 0 19 17.3 120	0 to 15 16 to 125	Unconfined aquifer Uppermost confined aquifer Lower confined aquifer Grande Ronde Basalt (RSH-1) Mabton Member Umtanum basalt (DC-6) ARRH-DC-1; 978 to 900 m	ARRHCO (1976) ARRHCO (1976) ARRHCO (1976) Deju (1978) Deju (1978) LaSala and Doty (1971)	III Fig. 5 7	18 50
Chloride	13 16 90 16.2 66.6 148 98	3.1 to 24 3.8 to 81 68 to 98	Unconfined aquifer Uppermost confined aquifer Lower confined aquifer Grande Ronde Basalt (RSH-1) Mabton Member Umtanum basalt ARRHDC-1; 978 to 990 m	ARRHCO (1976) ARRHCO (1976) ARRHCO (1976) Deju (1978) Deju (1978) LaSala and Doty (1971)	III Fig. 5 7	18 50
<p>*All values, except pH, are in mg/l.</p>						

TABLE A-II (continued)

TABLE A-11 (continued)						
PARAMETERS	AVERAGL VALUE*	RANGL OF VALUES*	REMARKS	DATA SOURCI AUTHOR (YEAR)	DATA SOURCE TABLE / PAGE	
Fluoride	39	37 to 41	Umtanum basalt (DC-6)	LaSala and Doty (1971)	7	50
	20		ARH-DC-1; 978 to 990 m			
Hardness, total	170	110 to 220 3 to 96	Unconfined aquifer	ARHCO (1976)	7	50
	66		Uppermost confined aquifer	ARHCO (1976)		
	2	Lower confined aquifers	ARHCO (1976)			
	35	Umtanum basalt (DC-6)				
	7	ARH-DC-1; 978 to 990 m	LaSala and Doty (1971)			
Iron	0.65		ARH-DC-1, 978 to 990 m	LaSala and Doty (1971)	7	50
Magnesium	12	7.1 to 14 0 to 11	Unconfined aquifer	ARHCO (1976)	III Fig. 5	18
	7		Uppermost confined aquifer	ARHCO (1976)		
	0.1	Lower confined aquifer	ARHCO (1976)			
	1.0	Grande Ronde Basalt (RSH-1)	Deju (1978)			
	0.5	Umtanum Basalt (DC-6)	Deju (1978)			
	0.1	Mabton Member				
	0.1	ARH-DC-1; 978 to 990 m	LaSala and Doty (1971)			
*All values, except pH, are in mg/l.						

TABLE A-II (continued)

PARAMETERS	AVERAGE VALUE*	RANGE OF VALUES*	REMARKS	DATA SOURCE AUTHOR (YEAR)	DATA SOURCE TABLE / PAGE	
Nitrate	0.2		ARRH-DC-1; 978 to 990 m	LaSala and Doty (1971)	7	50
pH*	8.0	7.5 to 8.1	Unconfined aquifer	ARHCO (1976)	7	50
	8.0	7.2 to 8.7	Upper confined aquifer	ARHCO (1976)		
	9.6	8.9 to 9.9	Lower confined aquifer	ARHCO (1976)		
	7.3		Grande Ronde Basalt (RSH-1)	Deju (1978)	III	
	8.6		Mabton Member	Deju (1978)	Fig. 5	18
	10	9.9 to 10.1	Umtanum basalt (DC-6)			
	9.9		ARRH-DC-1; 978 to 990 m	LaSala and Doty (1971)	7	50
Phosphate	0.2		ARRH-DC-1; 978 to 990 m	LaSala and Doty (1971)	7	50
Potassium	6.8	4.6 to 11	Unconfined aquifer	ARHCO (1976)		
	9.0	4.5 to 17	Uppermost confined aquifer	ARHCO (1976)		
	4.0	3.0 to 5.9	Lower confined aquifer	ARHCO (1976)		
	9		Grande Ronde Basalt (RSH-1)	Deju (1978)	III	
	13		Mabton Member	Deju (1978)	Fig. 5	18
	3.2		Umtanum basalt (DC-6)			
	5.9		ARRH-DC-1; 978 to 990 m	LaSala and Doty (1971)	7	50
*All values, except pH, are in mg/l.						

TABLE A-II (continued)

PARAMETERS	AVERAGE VALUE*	RANGE OF VALUES*	REMARKS	DATA SOURCE AUTHOR (YEAR)	DATA SOURCE TABLE / PAGE	
Silica (As Si)	22.5 31.9 53.8 105		Grande Ronde Basalt (RSH-1) Mabton Member Umtanum basalt (DC-6) ARH-DC-1; 978 to 990 m	Deju (1978) Deju (1978) LaSala and Doty (1971)	III Fig. 5 7	18 50
Sodium	29 40 168 30 110 242 176	16 to 64 4.1 to 122 134 to 182	Unconfined aquifer Uppermost confined aquifer Lower confined aquifers Grande Ronde Basalt (RSH-1) Mabton Member Umtanum basalt (DC-6) ARH-DC-1; 978 to 990 m	ARHCO (1976) ARHCO (1976) ARHCO (1976) Deju (1978) Deju (1978) Rockwell Hanford Operations (1979), Personal Communication LaSala and Doty (1971)	III Fig. 5 7	18 50
Sulfate	58 9 14 23 0.6 96 10	20 to 150 0 to 29 10 to 21	Unconfined aquifer Uppermost confined aquifer Lower confined aquifers Grande Ronde Basalt (RSH-1) Mabton Member Umtanum basalt ARH-DC-1; 978 to 990 m	ARHCO (1976) ARHCO (1976) ARHCO (1976) Deju (1978) Deju (1978) LaSala and Doty (1971)	III Fig. 5 7	18 50
*All values, except pH, are in mg/l.						

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APPENDIX B

THE MODIFIED MATERIALS
SELECTION PROCESS

APPENDIX B

THE MODIFIED MATERIALS
SELECTION PROCESS

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APPENDIX B
THE MODIFIED MATERIALS
SELECTION PROCESS

B.1 INTRODUCTION

This appendix documents the modified process for selecting candidate plug materials developed during the present studies. The original selection process was developed during earlier work and was described in Taylor and others (1979). The background and philosophy of the materials selection process is discussed in detail in Chapter 3 of this report. The objective of the materials selection process was to identify candidate materials for use in the testing programs; these materials have a high probability for successful use in plugs and a high probability of meeting projected NRC criteria and are considered suitable for use in advanced geochemical and physical testing programs.

The selection process presented here is an outgrowth of a re-evaluation of the materials selection process used in earlier work. This revised approach formally and systematically examines the material selection problem using decision analysis. The selection process evaluates candidate materials in sufficient detail so that the most appropriate materials, based on current information, are selected for testing. The procedure is documented in sufficient detail so that a revised analysis can be carried out if additional information becomes available on the materials being analyzed or if potentially useful new materials are identified.

This appendix is organized as follows: details of each step of the selection process and implementation of each step are described in Sections B.2 through B.8 and conclusions are discussed in Section B.9. A flowchart summarizing the materials selection process is shown in Figure B-1.

B.2 STEP 1: SELECTION OF MATERIALS FOR CONSIDERATION

As discussed in Chapter 3 of this report, the initial list of materials to be considered in Step 1 of the materials selection process was assembled by WCC personnel during Task I work and is shown in Table B-I. This list is modified during Step 3 (Section B.4) to remove any materials that are considered to be exclusively additives; only potential major plug components are being evaluated in this selection process. The list presented in Table B-I is not exhaustive; it is a sampling of material types rather than a complete list of every conceivable candidate material under a given classification. For instance, some natural materials on the list (such as the zeolite, clinoptilolite, or the crystalline rock, granite) are representatives of groups of minerals or rocks possessing particular properties. Likewise, manufactured items, such as concretes, are representative of a class of man-made materials that include many alternative choices. Various factors (such as availability) may make the alternate possibilities in each of the various classifications more desirable than the specific one currently listed. However, the process of listing representatives from these groups and comparing their characteristics suffices to discriminate between their relative desirability at the present level of study and plug design.

FIGURE B-1
MATERIAL SELECTION PROCESS

TABLE B-I

MATERIALS FOR CONSIDERATION*

Igneous and Metamorphic Rocks

Basalt
Granite
Natural glass
Slate
Serpentinite

Sedimentary Materials

Shale
Diatomaceous earth

Minerals

Quartz
Smectite clays
Vermiculite
Kaolinite
Illite
Talc
Clinoptilolite
Phillipsite
Magnetite
Hematite
Barite
Gypsum

Native Elements

Gold
Silver
Platinum
Carbon
Copper

Natural Organic Materials

Tar
Amber

Processed Metals

Lead
Metal alloys

Ceramics

Mullite
Steatite

Manufactured GlassesQuasi-Natural Materials

Fly ash

Synthetic Resins

Epoxy
Polyacrylamide
Phenoplast
Aminoplast
Polyester
Polyvinyl
Furnan compounds

SiliconesPolymersGrouts

Portland cements
Type I
Type II
Type V
Pozzolan
Hydrothermal cements
(calcium aluminate types)

Concretes

Portland cements plus
aggregate
Hydrothermal cements
plus aggregate

Asphalts

* Modified after Table B-II in Taylor and others (1979).

This initial list of materials is based on a literature review and on the judgment of knowledgeable individuals. If new materials that might be applicable to the the borehole plugging study become known during the program, they can be evaluated using the procedure presented in this appendix. The reader is referred to Chapter 3, Section 3.3.1, of this report for a more complete discussion of the development of the initial list of materials.

B.3 STEP 2: PRELIMINARY SCREENING

The preliminary screening (Step 2 in Figure B-1) eliminates from further consideration those materials that are unacceptable on the basis of chemical stability or documented survival history. Each of these properties alone is critical enough to the design and performance of a plug that a low rating for either one makes a material unacceptable, regardless of its other characteristics. The attributes used in this screening are discussed below, and specific scales used in the screening are presented in Table B-II.

B.3.1 Chemical Stability

Any material that is chemically unstable in environments characterized by pH levels of 7 to 10 and Eh levels of -0.2 volt or less is unacceptable because the natural geologic environment at the Hanford Site is basic and reducing in character. Thus, a rating of zero on the chemical stability attribute in Table B-II eliminates a material from further consideration.

TABLE B-II

PRELIMINARY SCREENING ATTRIBUTES^a

<u>Attribute</u>	<u>Scale</u>	<u>Description</u>
Chemical Stability ^b	0	Affected by pH 7 to 10 at Eh $\leq$ -0.2 volt
	1	Stable in pH 7 to 10 at Eh $\leq$ -0.2 volt
Documented History of Survival ^c	0	Less than a few thousand years of relevant documen- ted history of survival and no analogs of similar material in nature
	1	Man-made material; an analog or the actual material can be documented for thousands of years (on the order of the containment lifetime of the repository)
	2	Natural material; survival history of millions of years in nature

^a A rating of zero on either criterion is sufficient to eliminate a material from further consideration.

^b pH and Eh ranges determined from data in Table A-I, Appendix A, of this report.

^c Attribute ranges reflect the expected long-term containment lifetime of the repository as well as logical limits based on data for most categories of materials.

B.3.2 Documented Survival History

Materials used as plugs will be required to survive for thousands of years. Thus, conservative engineering practice dictates that only materials with a substantial documented history of survival be used in plug construction. It is unlikely that a material with an inadequately documented history of survival through time will be acceptable for use in plugs. The documented survival history screen eliminated any material with less than several thousand years of documented history for that material specifically or for a natural analog of the material (i.e., a rating of zero on the attribute for documented history of survival in Table B-II).

The ratings of individual materials were based on data that are currently available to WCC project staff and are included in publications listed as references to this appendix. The ratings are presented in Table B-III. Materials that survived the preliminary screening are listed in Table B-IV.

B.4 STEP 3: FUNCTION CLASSIFICATION

Candidate materials remaining after the preliminary screening were classified by three major functions: (1) to inhibit fluid flow; (2) to inhibit radionuclide migration; or (3) to provide structural integrity. Materials that could serve more than one function were classified under all relevant categories. These function classifications are described in more detail in Section 3.3.3 of this report.

This classification (Step 3 in the materials selection process) was necessary because the evaluation process was somewhat different for each category. In particular, the relevant material

TABLE B-III
RESULTS OF PRELIMINARY SCREENING

<u>Material</u>	<u>Chemical Stability^a</u>	<u>Documented History of Survival^b</u>	<u>Material</u>	<u>Chemical Stability</u>	<u>Documented History of Survival</u>
<u>Igneous and Metamorphic Rocks</u>			<u>Ceramics</u>		
Basalt	1	2	Mullite	1	1
Granite	1	2	Steatite	1	1
Natural glass	1	2	<u>Manufactured Glasses</u>		
Slate	1	2		1	1
Serpentine	1	2	<u>Quasi-Natural Materials</u>		
<u>Sedimentary Materials</u>			Fly ash	1	1
Shale	1	2	<u>Synthetic Resins</u>		
Diatomaceous earth	1	2	Epoxy	-	0
<u>Minerals</u>			Polyacrylamide	-	0
Quartz	1	2	Phenoplast	-	0
Smectite clays	1	2	Aminoplast	-	0
Vermiculite	1	2	Polyester	-	0
Kaolinite	1	2	Polyvinyl	-	0
Illite	1	2	Furnan compounds	-	0
Talc	1	2	<u>Silicones</u>		
Clinoptilolite	1	2		1	1
Phillipsite	1	2	<u>Polymers</u>		
Magnetite	1	2		-	0
Hematite	0	2	<u>Grouts</u>		
Barite	1	2	Portland cements		
Gypsum	1	2	Type I	1	1
<u>Native Elements</u>			Type II	1	1
Gold	1	2	Type V	1	1
Silver	1	2	Pozzolan	1	1
Platinum	1	2	Hydrothermal		
Carbon	1	2	cements (calcium		
Copper	1	2	aluminate types)	1	1
<u>Natural Organic Materials</u>			<u>Concretes</u>		
Tar	1	2	Portland cement		
Amber	1	2	plus aggregate	1	1
<u>Processed Metals</u>			Hydrothermal cement		
Lead	1	2	plus aggregate	1	1
Metal Alloys	1	2	<u>Asphalts</u>		
				1	0

^a Assignment of attribute value is principally based on references listed at the end of this appendix, in particular: Benson(1978), Clark(1966), Garrels and Christ(1965), Grim(1968), Kracek and Clark(1966), Krauskopf(1967), Sand and Mumpton(1978), Swedish Nuclear Fuel Safety Project(1977a and 1977b), Swineford(1957), Weant(1976), and Young(1947).

^b Assignment of attribute value is based on professional judgment.

TABLE B-IV

MATERIALS REMAINING AFTER PRELIMINARY SCREENING

<u>Igneous and Metamorphic Rocks</u>	<u>Natural Organic Materials</u>
Basalt	Tar
Granite	Amber
Natural glass	
Slate	<u>Processed Metals</u>
Serpentinite	Lead
	Metal alloys
<u>Sedimentary Materials</u>	
Shale	<u>Ceramics</u>
Diatomaceous earth	Mullite
	Steatite
<u>Minerals</u>	
Quartz	<u>Manufactured Glasses</u>
Smectite clays	
Vermiculite	<u>Quasi-Natural Materials</u>
Kaolinite	Fly ash
Illite	
Talc	<u>Silicones</u>
Clinoptilolite	
Phillipsite	<u>Grout</u>
Magnetite	Portland cements
Barite	Type I
Gypsum	Type II
	Type V
<u>Native Elements</u>	Pozzolan
Gold	Hydrothermal cements
Silver	(calcium aluminate types)
Platinum	
Carbon	<u>Concretes</u>
Copper	Portland cements plus
	aggregate
	Hydrothermal cements
	plus aggregate

properties that need to be considered while evaluating a material depend on the function for which the material will be used. Table B-V shows the relevant properties for each function. (The rationale for selecting these properties is discussed in Sections 3.3.5 and B.6 of this report). Table B-VI presents the list of materials according to function.

During function classification, it was determined that some of the materials that had initially been selected for consideration as possible plugging materials from the original list (modified from Taylor and others, 1979) in Step 1 of this selection process did not fit any of the three possible classifications for potential use in plugs. These materials were dropped from further consideration at this time. In general, these materials were initially considered because they provide shielding against radiation or could be mixed with other materials (such as cement) as additives to provide certain desirable properties. While radiation shielding may be desirable for repository backfill near storage canisters, it is not a necessary function for a borehole, shaft, or tunnel plug. In addition, the use of materials as additives will be examined on a case by case basis during pre-conceptual design and testing. The materials dropped from further consideration at this time are shown in Table B-VII.

B.5 STEP 4: DATA AVAILABILITY SCREENING

During pre-conceptual design and in the testing programs, materials will be evaluated on their suitability for plugs, based on how material properties affect their expected behavior over time in the natural geologic environment of the repository site. Materials for which a large data base has been accumulated are more predictable than are materials for which

TABLE B-V

RELEVANT MATERIAL PROPERTIES FOR EVALUATING MATERIALS*

<u>Function</u>	<u>Relevant Material Properties</u>
Inhibit fluid flow	Permeability Thermal Expansion
Inhibit radionuclide migration	Ion exchange potential Sorption capacity
Provide structural integrity	Strength Creep characteristics Thermal expansion

* Selection of material properties for each function classification is discussed in detail in Section 3.3.5 (Chapter 3) and Section B.6 (Appendix B) of this report.

TABLE B-VI
FUNCTION CLASSIFICATION OF MATERIALS

Materials to Inhibit Fluid Flow*	Materials to Inhibit Radionuclide Migration	Materials to Provide Structural Integrity
<u>Igneous and Metamorphic Rocks</u> Basalt Granite Natural glass Slate Serpentinite	<u>Igneous and Metamorphic Rocks</u> Basalt Serpentinite	<u>Igneous and Metamorphic Rocks</u> Basalt Granite Slate
<u>Sedimentary Materials</u> Shale	<u>Sedimentary Materials</u> Shale	<u>Minerals</u> Quartz
<u>Minerals</u> Quartz Smectite clays Vermiculite Kaolinite Illite Talc	<u>Minerals</u> Smectite clays Vermiculite Kaolinite Illite Talc Clinoptilolite Phillipsite	<u>Native Elements</u> Gold Silver Platinum Copper
<u>Native Elements</u> Gold Silver Platinum Carbon Copper	<u>Ceramics</u> Steatite	<u>Processed Metals</u> Lead Metal alloys
<u>Natural Organic Materials</u> Tar Amber		<u>Ceramics</u> Mullite Steatite
<u>Processed Metals</u> Lead Metal alloys		<u>Concretes</u> Portland cements plus aggregate Hydrothermal cements plus aggregate
<u>Ceramics</u> Mullite Steatite		
<u>Manufactured Glasses</u>		
<u>Silicones</u>		
<u>Grouts</u> Portland cements Type I Type II Type V Pozzolan Hydrothermal cements (calcium aluminate types)		
<u>Concretes</u> Portland cements plus aggregate Hydrothermal cements plus aggregate		

*Materials are assumed to be in a solid (crystalline), unmixed and uncrushed state.

TABLE B-VII

MATERIALS WHICH DO NOT FIT ONE OF THE
THREE FUNCTION CLASSIFICATIONS

Sedimentary Materials
Diatomaceous earth

Minerals
Magnetite
Barite
Gypsum

Quasi-Natural Material
Fly ash

fewer data are available. The data availability screen (Step 4) eliminated those materials for which data were judged inadequate (using university and company libraries, textbooks, scientific journals, and professional reports) to reliably evaluate the relevant properties within the time constraints of the testing program. For a material to pass this screen does not require that every property discussed under each function classification (Section B.6) be completely defined in the literature. Materials that are similar to other well-documented materials, or materials that have well-documented properties and are similar to those discussed in the next section, are considered as having sufficient, available information to be able to assign attribute values on the basis of professional judgment or analogy (as discussed in Section B.6.2). However, those materials that lack sufficient, pertinent data on properties of concern (see Section B.6) or lack well-documented analogs are eliminated by this screen. (See Section 3.3.4 for a more complete discussion of Step 4.)

The scale for assessing data availability is presented in Table B-VIII. In determining the ratings for individual materials, only the availability of data concerning the function(s) to be performed by the material (as specified in Section B.4) was considered. Thus, for example, only data on ion exchange capacity and sorption capacity were needed for materials that are to inhibit radionuclide migration. On the other hand, for a material that may provide structural integrity, it is necessary to have data on strength, creep characteristics, and thermal expansion.

Any material for which the relevant data base did not exist or could not be adequately determined within the time constraints of this study (i.e., receiving a rating of zero on the data

TABLE B-VIII
DATA AVAILABILITY ATTRIBUTE^a

<u>Attribute Name^b</u>	<u>Scale</u>	<u>Description</u>
Availability of relevant data	0	Relevant data applicable to program do not exist or cannot be adequately completed.
	1	Some data exist but must be supplemented with estimates.
	2	Most data exist, and only a few estimates are needed.

^aA rating of zero was sufficient to eliminate a material from further consideration.

^bRange of attribute values based on literature review and professional judgment.

availability attribute) was eliminated from further consideration. Ratings are presented in Table B-IX; the list of surviving candidate materials is presented in Table B-X.

B.6 STEP 5: DETERMINATION OF MATERIAL PROPERTIES AND ATTRIBUTE LEVELS

During Step 5 (discussed in this section) and Step 6 (discussed in Section B.7), the physical and chemical properties are evaluated for materials that were found in Step 3 to be potentially usable for one or more of the three functions in a plug. Subsequently, in Step 7 (discussed in Section B.8), the materials were further analyzed to select materials for pre-conceptual design that possess particular attributes indicating they should receive first priority for testing. The following questions are pertinent in developing the procedures used in Steps 5 and 6 of this selection process:

- What material properties should be considered?
- What attributes (evaluation measures) should be used to measure each important material property?
- How should the attribute levels be determined for each material?
- How should the different attributes be combined to arrive at a single overall evaluation of the physical and chemical properties of each material?

During Steps 5 and 6 of the materials selection process, it is not necessary to arrive at a specific ranking of the materials. Thus, a mathematical function that combines the

TABLE B-IX

RESULTS OF DATA AVAILABILITY SCREENING

Materials to Inhibit Fluid Flow		Materials to Inhibit Radionuclide Migration		Materials to Provide Structural Integrity	
<u>Material</u>	<u>Evaluation*</u>	<u>Material</u>	<u>Evaluation*</u>	<u>Material</u>	<u>Evaluation*</u>
Basalt	2	Basalt	2	Basalt	2
Granite	2	Serpentinite	1	Granite	2
Natural glass	2	Shale	1	Slate	2
Slate	2	Smectite clays	2	Quartz	2
Serpentinite	2	Vermiculite	2	Gold	2
Shale	2	Kaolinite	2	Silver	2
Quartz	2	Illite	2	Platinum	2
Smectite clays	2	Talc	1	Copper	2
Vermiculite	2	Clinoptilolite	2	Lead	2
Kaolinite	1	Phillipsite	2	Metal alloys	1
Illite	1	Steatite	1	Mullite	2
Talc	2			Steatite	2
Gold	2			Concretes	
Silver	2			(both types)	2
Platinum	2				
Carbon	1				
Copper	2				
Tar	1				
Amber	1				
Lead	2				
Metal alloys	1				
Mullite	1				
Steatite	1				
Manufactured glass	0				
Silicones	0				
Cements (all types)	1				
Concretes (both types)	1				

* Assignment of attribute value based on literature review and professional judgment.

TABLE B-X

MATERIALS REMAINING AFTER DATA AVAILABILITY SCREENING

<u>Materials to Inhibit Fluid Flow</u>	<u>Materials to Inhibit Radionuclide Migration</u>	<u>Materials to Provide Structural Integrity</u>
<u>Igneous and Metamorphic Rocks</u>	<u>Igneous and Metamorphic Rocks</u>	<u>Igneous and Metamorphic Rocks</u>
Basalt	Basalt	Basalt
Granite	Serpentinite	Granite
Natural glass		Slate
Slate	<u>Sedimentary Materials</u>	<u>Minerals</u>
Serpentinite	Shale	Quartz
<u>Sedimentary Materials</u>	<u>Minerals</u>	<u>Native Elements</u>
Shale	Smectite clays	Gold
	Vermiculite	Silver
<u>Minerals</u>	Kaolinite	Platinum
Quartz	Illite	Copper
Smectite clays	Talc	
Vermiculite	Clinoptilolite	<u>Processed Metals</u>
Kaolinite	Phillipsite	Lead
Illite		Metal alloys
Talc	<u>Ceramics</u>	
	Steatite	<u>Ceramics</u>
<u>Native Elements</u>		Mullite
Gold		Steatite
Silver		
Platinum		<u>Concretes</u>
Carbon		Portland cements plus aggregate
Copper		Hydrothermal cements plus aggregate
<u>Natural Organic Materials</u>		
Tar		
Amber		
<u>Processed Metals</u>		
Lead		
Metal alloys		
<u>Ceramics</u>		
Mullite		
Steatite		
<u>Grouts</u>		
Portland cements		
Type I		
Type II		
Type V		
Pozzolan		
Hydrothermal cements		
(calcium aluminate types)		
<u>Concretes</u>		
Portland cements plus aggregate		
Hydrothermal cements plus aggregate		

various attributes into a single number summarizing the desirability of a material is not required. Such a mathematical function would require assignment of specific relative importance weights to the various material properties, which would involve judgments about the relative importance for plug design of the various properties. These judgments would have to be based on assumptions about potential plug configurations. Because the plug is yet to be designed, such assumptions would be speculative and were avoided at this stage of the investigation.

B.6.1 Relevant Material Properties

A wide variety of chemical and physical properties is potentially relevant for evaluating the desirability of a material for use in borehole, shaft, or tunnel plugs. Selecting the appropriate properties for use here requires that the purpose of the material selection process, which is to select materials for inclusion in programs for continued evaluation and testing, be kept clearly in mind. Note that the purpose is not to make a final selection of materials for use in plugs or to select a design for a plug. Many properties of a material will be important in deciding on a specific plug design that best utilizes that material. However, during the initial evaluation of whether a material should be considered for use in a plug, it is deemed appropriate to consider only a few critical material properties that will be important regardless of the plug's exact design.

Physical and chemical properties were selected for each function classification to help characterize the suitability of materials that could conceivably meet the requirements of the classification. In each case, the list of selected properties

is based on parameters under each function classification for which adequate data exist in the literature and for which a direct evaluation can be made as to its impact on potential plug design.

Ambivalence surrounds the evaluation of certain properties as to their impact on the final performance of a plug. These properties were not used in the evaluation of materials under each function classification. Material properties used in the evaluation are discussed in the following sections. (In Chapter 3, Sections 3.3.5.1 to 3.3.5.3, the selection of material properties is discussed in more detail.)

B.6.1.1 Properties for Materials to Inhibit Fluid Flow

Permeability is the primary measure of the ability of a material to inhibit fluid flow. Many factors affect permeability, and a range of values for permeability is commonly cited in the literature for any given material. In addition, other physical properties of a material can directly affect the bulk permeability of a plug. One of these, thermal expansion, is included on the list of properties for materials to inhibit fluid flow which is shown in Table B-XI. Materials having coefficients of thermal expansion similar to basalt are considered more suitable for plugs than are materials with greatly different coefficients of thermal expansion because separation at the plug/wall rock interface and induced fracturing of the plug or basalt during the heating and cooling cycles of the containment period of a repository should be less likely if the plug has a coefficient of thermal expansion similar to basalt. Fracturing induced by materials having thermal expansion coefficients greatly different than basalt could drastically and adversely affect the bulk permeability of plugs.

TABLE B-XI

ATTRIBUTE SCALES FOR MATERIALS TO INHIBIT FLUID FLOW

<u>Attribute Name</u>	<u>Symbol</u>	<u>Attribute Scale</u>
Permeability*	F_1	<ol style="list-style-type: none"> 1. High (more than 10^{-6} cm/sec) 2. Moderate (10^{-6} to 10^{-8} cm/sec) 3. Low; in the range of basalt or less (less than 10^{-8} cm/sec)
Thermal Expansion*	F_2	<ol style="list-style-type: none"> 1. Significantly lower or higher than basalt 2. In the range of basalt ($6.6 \times 10^{-6}/^{\circ}\text{C}$) 3. Slightly greater than basalt (7×10^{-6} to $10^{-4}/^{\circ}\text{C}$)

* Attribute ranges determined from data in Table A-I, Appendix A, of this report.

Other potentially relevant factors, such as modulus of elasticity and plasticity index, were also considered, but the significance of these properties is difficult to determine unless a specific plug design is being evaluated. For instance, very high elasticity or plasticity can either be detrimental or beneficial in a plug material, depending on its proposed use. Both properties could influence the long-term ability of a plug to restrict fluid flow. However, because their impact is unclear (e.g., high plasticity may be desirable in some plug designs to maintain impermeability and undesirable in others), they are not used to evaluate materials at this time.

Thus, permeability and thermal expansion are the two factors that form the basis for determining the overall potential of a material for inhibiting fluid flow in this evaluation. The influence of thermal expansion on long-term permeability is reasonably direct and somewhat easier to infer than the effects of other factors, such as the modulus of elasticity and plasticity index. These latter factors have not been included here but should be considered once actual plug design is underway. Chemical stability and potential durability have already been assessed in Step 2.

B.6.1.2 Properties and Attributes of Materials for Inhibiting Radionuclide Migration

Under this function classification, the suitability of those materials that could inhibit the migration of radionuclides (although not necessarily a fluid containing them) was evaluated. In addition to low permeability, a large capacity to exchange ions with the environment is one important mechanism by which plug material can help control the migration of

radionuclides in solution; ion exchange potential and sorption capacity are two primary indicators of this ability.

Ion exchange potential is a measure of the ability of a material to set free and replace ions in its structure with ions in solution in contact with the material. Materials with high ion-exchange potentials may have the capacity for setting free ions from their lattice structure and replacing them with (and thus immobilizing) radionuclides.

Sorption capacity is a measure of the general ability of a material to entrap ions migrating in solution; the actual sorption mechanism for any given material can reflect several phenomena including: van der Waals bonding, the filling of vacant lattice spaces in crystal structure, and the entrapment of ions by the host due to unsatisfied bonds along crystal edges (edge effects), as well as actual ion exchange (as described above). Generally, the distribution coefficient (K_d) value, which gives a relative assessment of the sorption capacity of a material, is a collective, somewhat qualitative measure of these various phenomena.

Both ion exchange potential and sorption capacity are temperature dependent; for most materials, they decrease with increasing temperature. However, thermal stability is not included as a third attribute under this function classification because the temperature at plug seats is expected to be less than 100°C (see Table A-I, Appendix A). Within this temperature range, the ion exchange potentials and sorption capacities for most materials are not greatly affected, and thermally induced changes in the materials listed under this function classification are minor. Table B-XII lists the attribute scales applied to ion exchange potential

TABLE B-XII

ATTRIBUTE SCALES FOR MATERIALS
TO INHIBIT RADIONUCLIDE MIGRATION

<u>Attribute Name</u>	<u>Symbol</u>	<u>Attribute Scale</u>
Ion Exchange Potential*	R_1	<ol style="list-style-type: none"> 1. No or very low exchange potential 2. Low (5 to 40 mEq./100 g) 3. Moderate (40 to 80 mEq./100 g) 4. High (>80 mEq./100 g)
Sorption Capacity*	R_2	<ol style="list-style-type: none"> 1. No or very weak sorption capacity 2. Weak (K_d values <10 ml/g) 3. Moderate (K_d values = 10 to 100 ml/g) 4. Strong (K_d values >100 ml/g)
<hr/> <p>* Attribute ranges determined from high and low values published in reference cited with this appendix, in particular: Ames(1978); Barrer(1978); Fried and others (1978); Komarneni and Roy(1979); Ma and Lee(1978); Mercer and Ames(1978); Olson(1975); Sand and Mumpton (1978); Slemmons and Seyforth(1978); Swedish Nuclear Fuel and Safety Project(1977a and 1977b); Swineford (1957); and Tsitsishvili(1978). K_d values (as used here) reflect generalizations, and materials are assigned attribute levels on the basis of their ability to sorb various (but not all) radionuclides of concern. Thus, the ability to sorb any radionuclide qualifies a material as possessing this attribute.</p>		

and sorption capacity, the two properties used to rank a material's ability to inhibit radionuclide migration in this selection process. Chemical stability has already been assessed in Step 2.

B.6.1.3 Properties of Materials for Providing Structural Integrity

Structural integrity of the plug will be provided primarily by its ability to resist or accommodate deformation over time due to tectonism, heating and cooling of the repository, lithostatic pressure, and hydrostatic pressure. Because of the possible easy deformation of materials that provide the other important functions of inhibiting fluid flow and radionuclide migration, it was deemed necessary to evaluate separately materials suitable for providing the plug with requisite strength during the containment period of the repository. While deformable, plastic materials will provide some physical continuity in large openings (shafts and tunnels); such materials may need to be buttressed by more rigid plug components capable of transmitting various loads that may be imposed on large plugs. Thus, the factors listed in Table B-XIII for evaluating the ability of a material to provide structural integrity include strength (in unconfined compression), creep (as a measure of a material's long-term behavior), and its coefficient of thermal expansion.

The last factor measures the compatibility of the candidate plug material with host rock and the natural environment. Materials that have thermal expansion properties similar to those of basalt are preferred. Chemical stability and potential durability have already been assessed in Step 2.

TABLE B-XIII

ATTRIBUTE SCALES FOR MATERIALS
TO PROVIDE STRUCTURAL INTEGRITY

<u>Attribute Name</u>	<u>Symbol</u>	<u>Attribute Scale</u>
Strength in unconfined compression*	P_1	1. Low (<25 MPa) 2. Medium (50 to 150 MPa) 3. High (same order as basalt [150 to 300 MPa])
Creep characteristics*	P_2	1. High ($>10^{-10}$ /sec) 2. Moderate (10^{-10} to 10^{-15} /sec) 3. Low (in the range of basalt at the plug seat depths and expected temperatures [$>10^{-15}$ /sec])
Thermal expansion*	P_3	1. Significantly lower or higher than basalt 2. In the range of basalt ($6.6 \times 10^{-6}/^{\circ}\text{C}$) 3. Slightly greater than basalt (7×10^{-6} to $10^{-4}/^{\circ}\text{C}$)
* Attribute ranges determined from data in Table A-I, Appendix A, of this report.		

B.6.2 Attribute Levels for Materials

In order to determine and record material properties in a consistent and easily understandable way, numerical evaluation measures (attributes) were used to summarize the properties of each material. The assignment of attribute levels to materials listed in Table B-XIV was based on three steps. The selection of appropriate ranges for the attribute scales, as listed in Tables B-XI to B-XIII, was the first step. These ranges reflect either information on the natural environment (taken from Table A-I in Appendix A of this report) or were selected using naturally occurring materials for which information is available (see references to this appendix) to help scale the attribute. For instance, the scaling of ion exchange potential reflects values published in the literature for materials with a notably high ion exchange potential as compared to materials with progressively lower ion exchange potentials.

The second step was to tabulate all readily available data concerning the various materials and respective properties. In most cases, ranges in published data for the properties of a given material fall within the range of a defined level for each of the various attribute scales. The references used in this step are listed with this appendix. The pertinent material properties for all the candidate plug materials are shown in Table B-XIV.

Because not every property listed as an attribute has been measured for every material listed in Table B-XIV (or because the pertinent data could not be located in the available time), the third step in determining attribute levels was, where necessary, to assign levels on the basis of analogy with

TABLE B-XIV

PROPERTIES OF CANDIDATE MATERIALS

<u>Materials to Inhibit Fluid Flow^a</u>		
<u>Material</u>	<u>Permeability^b</u>	<u>Thermal Expansion^b</u>
<u>Igneous and Metamorphic Rocks</u>		
Basalt	3	1/2
Granite	3	2
Natural glass	3	2
Slate	3	2
Serpentine	3	3
<u>Sedimentary Materials</u>		
Shale	3	3
<u>Minerals</u>		
Quartz	3	3
Smectite clays	3	3
Vermiculite	3	3
Kaolinite	3	2
Illite	2	2
Talc	3	3
<u>Native Elements</u>		
Gold	3	1
Silver	3	1
Platinum	3	1
Carbon	3	2
Copper	3	1
<u>Natural Organic Materials</u>		
Tar	3	1
Amber	3	1
<u>Processed Metals</u>		
Lead	3	1
Metal alloys	3	1
<u>Ceramics</u>		
Mullite	3	2
Steatite	3	2
<u>Grouts</u> (all types)	3	2
<u>Concretes</u> (both types)	3	2

^a Materials are assumed to be in a solid (crystalline), unmixed and uncrushed state.

^b Assignment of attribute values are based on the following references cited for this appendix: Brewer(1967); Cedergren(1967); Colorado School of Mines(1978;1979); Eilers and Spangle(1973); Grim(1968); Holliday(1966); Laguros(1969); Lama and Vutukuri (1978); Lambe and Whitman(1969); Merritt(1976); Mitchell(1976); Neville(1971); Pusch(1979); Root and Calvert(1971); Swineford (1957); Weant(1976); and Young(1947).

TABLE B-XIV (continued)

<u>Materials to Inhibit Radionuclide Migration</u>		
<u>Material</u>	<u>Ion Exchange Potential*</u>	<u>Sorption Capacity*</u>
<u>Igneous and Metamorphic Rocks</u>		
Basalt	1	3
Serpentinite	1	3
<u>Sedimentary Materials</u>		
Shale	2	3
<u>Minerals</u>		
Smectite clays	4	4
Vermiculite	4	4
Kaolinite	2	3
Illite	2	2
Talc	2	2
Clinoptilolite	4	4
Phillipsite	4	4
<u>Ceramics</u>		
Steatite	1	1

* Assignment of attribute value based on the following references cited for this appendix: Ames(1978); Barrer (1978); Fried and others(1978); Komarneni and Roy(1979); Ma and Lee(1978); Mercer and Ames(1978); Olson(1975); Sand and Mumpton(1978); Slemmons and Seyforth(1978); Swedish Nuclear Fuel and Safety Project(1977a and1977b); Swineford(1957); and Tsitsishvili(1978).

TABLE B-XIV (continued)

<u>Materials to Provide Structural Integrity^a</u>			
<u>Material</u>	<u>Strength^b</u>	<u>Creep Characteristics^b</u>	<u>Thermal Expansion^b</u>
<u>Igneous and Metamorphic Rocks</u>			
Basalt	3	3	2
Granite	3	3	2
Slate	2	3	2
<u>Minerals</u>			
Quartz	3	3	2
<u>Native Elements</u>			
Gold	3	1	1
Silver	3	1	1
Platinum	3	1	1
Copper	3	1	1
<u>Processed Metals</u>			
Lead	2	1	1
Metal alloys	3	1	1
<u>Ceramics</u>			
Mullite	3	3	2
Steatite	3	3	2
<u>Concretes</u>			
(both types)	2	3	2

^aMaterials are assumed to be in a solid (crystalline), unmixed and uncrushed state.

^bAssignment of attribute value based on the following references cited for this appendix: Agapito and others (1977); Alliot and Boehler (1979); Barla and Innurato (1973); Boa (1978); Brewer (1967); Clark (1966); Colorado School of Mines and Geology (1978; 1979); Eilers and Spangle (1973); Farmer (1968); Hoadley (1964); Holliday (1966); Lama and Vutukuri (1978); Merritt (1976); Neville (1971); Root and Calvert (1971); Weant (1976); and Young (1947).

similar materials for which data are available. In other cases, attributes were assigned on the basis of judgment and the expected behavior of a given material. Again, the primary objective of the materials selection process was to select preferred and promising materials for future study, and the judgmental assignments of attribute levels were considered accurate enough to meet this objective and to allow comparisons with attribute levels assigned on the basis of data collected during the second step. Because materials for which little data are available were screened out in Step 4, determination of the attribute level for each material using the various attribute scales was relatively straightforward. Within the level of detail used in this evaluation, there was no significant uncertainty about what the attribute levels were for a particular material.

B.7 STEP 6: EVALUATION OF PHYSICAL AND CHEMICAL PROPERTIES OF MATERIALS

To evaluate the overall physical and chemical properties of a material, it is necessary to consider all of the relevant properties of the material together. To the extent possible, it is desirable to evaluate candidate plug materials without deciding on the relative importance of the various attributes. This is desirable because the importance of the different factors depends in part on features of plug design that have not yet been determined. For example, the importance that should be attached to having high ion exchange potential depends on the degree to which this mechanism will be used to trap radionuclides in the plug. This has not yet been determined.

In order to avoid the subjective assignment of relative importance weights, a dominance analysis was carried out in Step 6. One material is said to dominate a second material if it has at least as high a rating as the second material on all relevant attributes (which numerically quantify a material's properties) and has a higher rating on at least one of the attributes. Because the attributes numerically summarize the material characteristics that are relevant for evaluation purposes, a material that dominates a second material is more preferable than the second material, regardless of what function is used to combine the attributes into a single measure of overall desirability.

The dominance analysis of the materials in each function classification had two steps: (1) The dominance relation (or lack of one) was identified between each pair of materials in each function classification (discussed in Section B.4) using the definition of dominance presented in Section B.7.1.1 (below); and (2) This information was used to determine a rank-ordering of the materials by applying an analysis method developed especially for this problem. In general, it is not possible to determine a complete ordering based only on dominance analysis. However, the analysis provided sufficient ranking for the evaluation in Step 6.

The basic idea of the analysis procedure can be illustrated by a simple example. Suppose five materials M_1 , M_2 , M_3 , M_4 , and M_5 are to be evaluated. Suppose that when the material property attributes are compared, it is found that M_1 dominates M_3 , M_4 , and M_5 ; M_2 dominates M_3 , M_4 , and M_5 ; M_3 dominates M_5 ; and M_4 dominates M_5 . These dominance relations are shown graphically in Figure B-2 in which the convention is used that a material at the tail of any arrow dominates any material

FIGURE B-2
EXAMPLE OF DOMINANCE RELATIONS

that can be reached by following a path in the direction of the arrows. Thus, for example, Figure B-2 shows that M_1 dominates M_5 because M_5 can be reached from M_1 by following the path M_1 to M_3 and M_3 to M_5 (or M_1 to M_4 and M_4 to M_5). Thus, Figure B 2 shows that the five materials can be categorized into three groups: M_1 and M_2 are more preferable than any of the other materials; M_3 and M_4 are less preferable than M_1 and M_2 but more preferable than M_5 ; and M_5 is least preferable of all the materials. Using only dominance, it is not possible to rank order M_1 and M_2 , nor is it possible to rank order M_3 and M_4 . Note, however, that this ranking does not necessarily mean that M_1 and M_2 are equally preferable or that M_3 and M_4 are equally preferable. Rather, the ordering of these pairs depends specifically on what function is used to combine their various attributes to determine their overall desirability.

Figure B-2 illustrates the basic idea underlying the dominance analysis used in Step 6 of the materials selection process; however, it is time-consuming to draw such a figure when there are more materials. Furthermore, in a more complex case, it is difficult to identify the rank-ordering that is implied by the diagram. For these reasons, an alternative approach for identifying the rank-ordering was developed for the modified selection process described here. This approach is presented in Section B.7.1, and the results of applying it are given in Section B.7.2.

B.7.1. Dominance Analysis Procedure

In this section, X_i will represent an attribute, and x_i will represent a specific level of X_i . For this presentation, it will not be necessary to distinguish whether the attributes are

being used to evaluate materials to inhibit fluid flow, inhibit radionuclide migration, or provide structural integrity.

B.7.1.1 Definition A-1 (Dominance)

Material m dominates material n if

$$\begin{aligned} x_i(m) &\succeq x_i(n), \text{ for all } i, \text{ and} \\ x_i(m) &> x_i(n), \text{ for some } i, \end{aligned}$$

where, $x_i(m)$ and $x_i(n)$, respectively are the ratings of the materials m and n on the i^{th} attribute, and $\succeq$ means "at least as preferable as," while $>$ means "preferable to."

Simply stated, dominance means that a material has at least as desirable levels on all attributes and has a more desirable level on at least one attribute. Clearly, the dominating material is more desirable than the dominated material.

B.7.1.2 Definition A-2 (Set Dominance)

For two subsets of materials M and N, M dominates N if, for any m in M, n in N,

$$\begin{aligned} x_i(m) &\succeq x_i(n), \text{ for all } i, \text{ and} \\ x_i(m) &> x_i(n), \text{ for some } i. \end{aligned}$$

In other words, the set of materials M is said to dominate the set N only if every material in M dominates every material in N. From the earlier discussion of dominance relations between pairs of materials it is clear that if M dominates N, then any material in M is more preferred than any material in N.

Set dominance concepts permit the identification of subsets M_1 , M_2 , ..., M_n ; M_1 dominates all the other subsets, M_2 dominates all other subsets except M_1 , M_3 dominates all the other subsets except M_1 and M_2 , and so forth. From the discussion above, it follows that each material in M_1 will be more preferable than any material in the other subsets, each material in M_2 will be less preferable than any material in M_1 and will be more preferable than any material in M_3 , M_4 , ..., M_n , and so forth. Based only on dominance concepts, it is not possible to rank-order the materials in any M_i .

B.7.1.3 Set Dominance Analysis Procedure

The procedure below can be used to identify the subsets M_1 , M_2 , ..., M_n . An example showing how the procedure is carried out is shown in Table B-XV, and a proof that the procedure works is given in Section B.7.1.4.

- (1) Using Definition A-1, identify all of the dominance relations between pairs of materials. Prepare a pairwise dominance relation table like Table B-XVa showing the pairwise dominance relation as follows:
 - a) List the materials in the same order down the left-hand side and across the top; and
 - b) Enter a 1 in a cell of the table if the row material dominates the column material; otherwise enter a 0.
- (2) Determine the total of each column and list it at the bottom of the column. This tells how many other materials dominate the material in that column.

TABLE B-XV

SET DOMINANCE ANALYSIS EXAMPLE

(a) Pairwise Dominance Relations

	M ₁	M ₂	M ₃	M ₄	M ₅	M ₆
M ₁	0	0	1	1	1	1
M ₂	0	0	1	1	1	1
M ₃	0	0	0	0	1	1
M ₄	0	0	0	0	0	1
M ₅	0	0	0	0	0	1
M ₆	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>
Column Totals	0	0	2	2	3	5

(b) Set Dominance Analysis

Required Number of Materials	Column Totals	Materials with Column Totals	Number of Materials with Column Totals	Cumulative Number of Materials with Column Totals
1	5	M ₆	1	1
2	4	--	0	1
3	3	M ₅	1	2
4	2	M ₃ , M ₄	2	4
5	1	--	0	4
6	0	M ₁ , M ₂	2	6

(3) Prepare a set dominance analysis table like Table B-XVb as follows:

- a) In the first column (Required Number of Materials), enter the numbers 1, 2, ..., m, where m is the total number of materials.
- b) In the second column (Column Total), enter the numbers m-1, m-2, ..., 2, 1, 0.
- c) In the third column (Materials with Column Total), list next to each number in the second column all the materials with that "Column Total" on the pairwise dominance analysis table.
- d) In the fourth column (Number of Materials with Column Total), enter next to each list of materials in the third column the number of materials in the list. (Note that the sum of all the entries in the fourth column is m.)
- e) In each row of the fifth column (Cumulative Number of Materials with Column Total), enter the sum of the entries in the fourth column down to and including that row.

(4) Identify the dominance relations as follows:

- a) Compare the entries in each row of the first and fifth columns of the set dominance analysis table. Draw a dashed line across the table under each row where the entries in the first and fifth columns are equal.

- b) From the third column of the table (Materials with Column Total), determine the sets of materials falling between successive pairs of dashed lines.
- c) These sets of materials are successively more preferable in the course down the set dominance analysis table. Within each set, it is not possible to determine the order of preference using only dominance concepts.

This analysis procedure is somewhat cumbersome to write down but is straightforward to carry out. For the example in Table B-XV, material m_6 is the least preferable; materials m_3 , m_4 , and m_5 are next most preferable; and materials m_1 and m_2 are most preferable. Based only on dominance arguments, it is not possible to determine which of the materials m_3 , m_4 , or m_5 is most preferable or least preferable. Similarly, it is not possible to determine which of m_1 or m_2 is more preferable.

B.7.1.4 Proof that Procedure Identifies $M_1, M_2, \dots, M_n$

The proof proceeds in two steps: (1) it is established that the subsets of materials between successive dashed lines are increasingly preferable as one works down the set dominance analysis table; and (2) it must be shown that the establishment of a complete preference order is not possible within the subset of materials between two successive dashed lines.

To establish that the subsets of materials between successive dashed lines are successively more preferable, it is sufficient to show that any material below any particular dashed line is more preferable than any material above the dashed line.

If there is a total of m materials, then from the definitions of Column 1 (Required Number of Materials) and Column 2 (Column Total), the sum of the entries in these two columns for any row will be m . Thus, if the "Column Total" immediately above a dashed line is n , the "Required Number of Materials" corresponding to this must be $m-n$. Given this information, it follows from the procedure used to construct the dashed line that all materials above the line are dominated by at least n materials, and there are exactly $m-n$ materials above the line (and hence, exactly n materials below the line).

All materials below the line can be less preferable than at most $n-1$ other materials. The rationale for this is as follows: Suppose one of the materials below the line is less preferable than at least n other materials. There must be exactly n materials that are less preferable than at most $n-1$ other materials. Hence, one of the materials above the line would have to be less preferable than at most $n-1$ other materials if one of the materials below the line is less preferable than at least n other materials. However, this is a contradiction because all materials above the line are dominated by at least n other materials. Hence, all materials below the line can be less preferable than at most $n-1$ other materials.

Because of this, each of the materials below the line must be more preferable than any material above the line. The rationale for this is as follows: Suppose a material below the line were not more preferable than some specified material above the line. Then, because the specified material above the line is less preferable than at least n other materials, the material below the line would also have to be less preferable

than at least n other materials. However, it has been shown above that each material below the line is less preferable than at most $n-1$ other materials. Hence, a contradiction has been established, and it must be true then that any material below the line is more preferable than any material above the line.

This establishes the first part of the proof. The remaining part to be established is that it is not possible to completely order the materials between any two dashed lines.

From the construction procedure, it follows that either there is only one material between a pair of successive dashed lines (in which case this part of the theorem is not applicable) or there must be at least two materials in the row immediately above the dashed line. However, it must be true then that none of the entries in this row dominates any other entry. The rationale for this is as follows: If one entry dominated another, then it would have a "Column Total" that was greater; hence, the two entries would not appear in the same row.

Because none of the entries in the row dominates another in the row, the preference order of the entries will depend on the particular preference structure used to evaluate the materials. Thus, the materials can not be ordered solely on the basis of set dominance analysis.

This establishes that the set dominance analysis procedure has the claimed properties.

B.7.2 Results of Evaluation of Physical and Chemical Properties of Materials

The results of analyzing the dominance relations between all pairs of materials in each of the three functional categories are shown in Tables B-XVI, B-XVII, and B-XVIII. These tables were prepared by applying Step 1 in the set dominance analysis procedure (discussed in Section B.7.1) to the data in Table B-XIV. The materials grouped together as a set in each table have exactly the same levels of all the relevant attributes. Thus, regardless of what procedure was used to combine the various attributes to evaluate the overall physical and chemical properties of the materials, it would not be possible to distinguish between the materials in any one set. Thus, for example, the materials in the set containing basalt, granite, quartz, mullite, and steatite have identical structural integrity attribute levels.

The results of carrying out the set dominance analysis on the data in Tables B-XVI, B-XVII, and B-XVIII are shown in Tables B-XIX, B-XX, and B-XXI.

B.8 STEP 7: CONSIDERATION OF OTHER FACTORS

The relative desirability of materials from the list in Table B-XIV (as presented in Tables B-XIX, B-XX, and B-XXI) is based only on the attributes listed in Tables B-XI to B-XIII. Prior to compilation of Table B-XIV, other important attributes, such as durability through time and chemical stability in the natural environment, had already been evaluated in Step 2 (discussed in Section B.3) for the materials that appear in Tables B-XIX, B-XX, and B-XXI. Other significant factors are considered in this section to aid in selecting a final list of

TABLE B-XVI

PAIRWISE DOMINANCE ANALYSIS OF MATERIALS
TO INHIBIT FLUID FLOW

	Basalt, granite, natural glass, slate, kaolinite, carbon, mullite, steatite, grouts, concretes	Serpentinite, shale, quartz, smectite clays, vermiculite, talc	Illite	Gold, silver, platinum, copper, tar, amber, lead, metal alloys
Basalt, granite, natural glass, slate, kaolinite, carbon, mullite, steatite, grouts, concretes			1	1
Serpentinite, shale, quartz, smectite clays, vermiculite, talc	1		1	1
Illite				
Gold, silver, platinum, copper, tar, amber, lead, metal alloys				
Column Totals	1	0	2	2
<p>1: Material in row dominates material in column.</p> <p>blank: Material in row does not dominate material in column.</p>				

TABLE B-XVII

PAIRWISE DOMINANCE ANALYSIS OF MATERIALS
TO INHIBIT RADIONUCLIDE MIGRATION

	Basalt, serpentine	Shale, kaolinite	Smectite clays, vermiculite, clinoptilolite, phillipsite	Illite, talc	Steatite
Basalt, serpentine					1
Shale, kaolinite	1			1	1
Smectite clays, vermiculite, clinoptilolite, phillipsite	1	1		1	1
Illite, talc					1
Steatite					
Column Totals	2	1	0	2	4
<hr/> <p>1: Material in row dominates material in column. blank: Material in row does not dominate material in column.</p>					

TABLE B-XVIII

PAIRWISE DOMINANCE ANALYSIS OF MATERIALS
TO PROVIDE STRUCTURAL INTEGRITY

	Basalt, granite, quartz, mullite, steatite	Slate, concretes	Gold, silver, platinum, copper, metal alloys	Lead
Basalt, granite, quartz, mullite, steatite		1	1	1
Slate, concretes				1
Gold, silver, platinum, copper, metal alloys				1
Lead				
Column Totals	0	1	1	3
<hr/> <p>1: Material in row dominates material in column. blank: Material in row does not dominate material in column</p>				

TABLE B-XIX
RESULTS OF SET DOMINANCE ANALYSIS OF
MATERIALS TO INHIBIT FLUID FLOW

Materials with most preferable physical and chemical properties	Serpentinite, shale, quartz, smectite clays, vermiculite, talc
Materials with second most preferable physical and chemical properties	Basalt, granite, natural glass, slate, kaolinite, carbon, mullite, steatite, grouts, concretes
Materials with third most preferable physical and chemical properties	Illite, gold, silver, platinum, copper, tar, amber, lead, metal alloys

TABLE B-XX

RESULTS OF SET DOMINANCE ANALYSIS OF
MATERIALS TO INHIBIT RADIONUCLIDE MIGRATION

Materials with most preferable physical and chemical properties	Smectite clays, vermiculite, clinoptilolite, phillipsite
Materials with second most preferable physical and chemical properties	Shale, kaolinite
Materials with third most preferable physical and chemical properties	Basalt, serpentine, illite, talc
Materials with fourth most preferable physical and chemical properties	Steatite

TABLE B-XXI

RESULTS OF SET DOMINANCE ANALYSIS OF
MATERIALS TO PROVIDE STRUCTURE INTEGRITY

Materials with most preferable physical and chemical properties	Basalt, granite, quartz, mullite, steatite
Materials with second most preferable physical and chemical properties	Slate, concretes, gold, silver, platinum, copper, metal alloys
Materials with third most preferable physical and chemical properties	Lead

preferred candidate materials for use in testing programs and preconceptual plug design.

The reasons that the various cost and availability issues considered in this step are evaluated after the physical and chemical properties of the materials are discussed in detail in Sections 3.2.2.4 and 3.3.7 of Chapter 3. The purpose of this step is primarily to determine whether cost and availability could change the order of the materials as shown in Tables B-XIX, B-XX, and B-XXI.

The factors considered in Step 7 included relative cost, availability, and applicability to small openings (boreholes) and/or large openings (tunnels and shafts). The materials are reviewed in generic groups to facilitate discussion and comparison of like entities. Qualitative statements about the physical and chemical properties of the materials are made in several places. The reader may wish to refer to Tables B-XIX, B-XX, and B-XXI to verify these statements.

B.8.1 Consideration of Other Factors for the Generic Group--Rocks

B.8.1.1 Basalt

Basalt mined from the repository and from access shafts and tunnels will supply a low cost, readily available material with low permeability, if used in solid machined plugs for small holes. It also has properties that make it desirable for use in functions requiring good strength to provide structural integrity for both solid plugs in small boreholes and, when crushed, for use in mixtures placed in tunnels and shafts. Basalt has a low ion exchange potential and sorption capacity

when compared with other materials, but a greater ability to inhibit radionuclide migration than most other rock types considered here. For all these reasons, it is included as a preferred candidate material.

B.8.1.2 Granite and Slate

These rocks have properties similar to basalt as to permeability and application in engineered fills. However, they are less readily available and would undoubtedly cost more than basalt in actual plugging applications. Because basalt would fulfill the same functions at lower cost, they are not included on the preferred list.

B.8.1.3 Serpentinite, Shale, and Natural Glass

These materials, if properly selected and placed, could conceivably have somewhat lower permeabilities than basalt and ion exchange potentials and could have sorption capacities equal to or slightly higher than basalt. However, they rank lower than basalt as to properties that would provide structural integrity and strength for plugs, and rank considerably lower than other materials in inhibiting fluid flow and radionuclide migration. Because other materials excel them in each function classification they are not included as preferred candidate plug materials.

B.8.2 Consideration of Other Factors for the Generic Group -- Minerals

B.8.2.1 Quartz

As can be seen in Tables B-XIX, B-XX, and B-XXI, a solid quartz plug machined to fit a small borehole has the property of low

permeability and the potential for providing good structural integrity. It compares favorably with basalt in these aspects and may even be somewhat more stable than basalt in the potentially changing chemical environment of the repository and boreholes. Crushed and used as a plug component in large openings such as shafts and tunnels, quartz would have properties similar to crushed basalt. However, it has no ion exchange potential or sorption capacity and would be somewhat more expensive than the readily available basalt in this application. Quartz is placed on the preferred materials list as a potential solid plug material for use in small boreholes only.

B.8.2.2 Smectite Clays, Vermiculite, and Kaolinite

Smectite clays and vermiculite both have excellent properties for inhibiting fluid flow and radionuclide migration. However, smectite clays (notable deposits of bentonite) are more readily available in the region surrounding the Hanford Site, and for this reason are preferred over vermiculite, which would prove more costly and difficult to acquire for use in plugging. Kaolinite has a moderate ability to block radionuclide migration and a relatively low potential permeability. Kaolinite and vermiculite are not included with smectite clays as preferred candidate plug materials for the reasons given above. However, because of the ability of kaolinite to trap anions migrating in solution and vermiculite's high ranking in most respects, both should be considered for possible use in specialized requirements of future plug designs.

B.8.2.3 Clinoptilolite and Phillipsite

Both of these zeolite minerals have very high ion exchange potentials and sorption capacities, and thus should excel in their ability to block radionuclides migrating in solution. Within several hundred kilometers of the Hanford Site are naturally occurring deposits of clinoptilolite; therefore, it was chosen for inclusion as the preferred candidate plug material over phillipsite on a cost basis.

B.8.2.4 Illite and Talc

These two materials have some ion exchange potential and sorption capacity, and talc has the potential for relatively low permeability in certain plug designs. However, other materials are better able to inhibit fluid flow and radionuclide migration; therefore illite and talc are not included as preferred candidate plug materials.

B.8.3 Consideration of Other Factors for the Generic Group -- Native Elements and Metals

B.8.3.1 Gold, Silver, Platinum, Copper, Lead, and Metal Alloys

These materials have low permeability and relatively high strength, which at first glance would appear to make them viable candidates as solid plugs for small boreholes. However, problems with shrinkage upon cooling after placement in a molten form and a coefficient of thermal expansion considerably different from that of basalt could conceivably degrade the bulk permeability of the plug system with time. In addition, all are considerably more costly than other materials being considered for solid plugs, and some (notably silver and

copper) may be somewhat unstable in the potentially changing chemical environment of repository boreholes and exploratory holes. Thus, none of the metals are included as preferred candidate plug materials.

B.8.3.2 Carbon

Very dense, pre-compacted carbon has potential use as a solid plug in a small hole. It would have relatively low permeability and possibly some ability to absorb migrating radionuclides. However, other materials in each function classification excel carbon in potential applications, and so it is not included as a preferred candidate plug material.

B.8.4 Consideration of Other Factors for the Generic Group -- Natural Organic Material

B.8.4.1 Tar and Amber

These organic materials, though impermeable, may become chemically unstable during the containment period of the repository and are not included as preferred candidate plug materials.

B.8.5 Consideration of Other Factors for the Generic Group -- Ceramics

B.8.5.1 Mullite and Steatite

Solid ceramic plugs manufactured to fit in small holes would have properties similar to solid basalt or quartz plugs with respect to their ability to inhibit fluid flow and provide structural integrity. Cost and availability would probably be

similar to that for machining solid basalt or quartz plugs. Steatite has minor ion exchange potential and sorption capacity and because of its other properties is included as a representative of this group of materials in the list of preferred candidate plug materials while mullite is not included.

B.8.6 Consideration of Other Factors for the Generic Group -- Grouts

B.8.6.1 Portland Cements and Hydrothermal Cements

These manufactured materials have relatively low permeability when compared with other materials considered in Table B-XIX. Because of their versatility, low cost, and general availability, they are included as preferred candidate plug materials.

B.8.7 Consideration of Other Factors for the Generic Group -- Concretes

B.8.7.1 Portland Cements plus Aggregate and Hydrothermal Cements plus Aggregate

When properly prepared and placed, concretes have relatively low permeability (and thus, some ability to block migrating fluids) and relatively high strength (to provide plugs with structural integrity). They appear to be potentially stable in the plug environment, and because of their low cost relative to other materials, versatility, and availability, concretes are included as preferred candidate plug materials.

B.8.8 Discussion

The final list of preferred materials is shown in Table B-XXII. Those materials set aside at this time are shown in Table B-XXIII. Note in particular that the preferred candidate plug materials listed in Table B-XXII all ranked in the most preferable category in Step 6 for at least one function classification, except grouts and concretes. These rank in the second most preferable category for at least one function classification, and were included because of various desirable cost and availability characteristics, as discussed in Sections B.8.6 and B.8.7.

Generally speaking, the materials set aside at this time (Table B-XXIII) ranked below the most desirable category in Step 6 in all function classifications. Exceptions to this are granite, serpentinite, shale, vermiculite, and mullite. These materials were set aside, even though they had desirable physical and chemical properties, because some other material included in the preferred candidate plug material list was judged to have at least as desirable properties and to be more practical or available, as discussed in the preceding sections.

B.9. CONCLUDING REMARKS

The seven-step materials selection process described in this appendix addresses the following questions:

- Is there adequate assurance that each selected material will survive and continue to perform as desired for the required length of time? (addressed in Step 2);

TABLE B-XXII
PREFERRED CANDIDATE PLUG MATERIALS

Material	Attributes
Basalt	Relatively impermeable as a solid plug. Good strength for engineering purposes. Low (but some) ion exchange potential and moderate sorption capacity. Low cost, high availability.
Quartz (only as a solid plug for small boreholes)	Impermeable. Good strength. Chemically stable. Low cost.
Smectite clays	Very impermeable. High ion exchange potential and sorption capacity. Chemically stable. Low cost, readily available
Clinoptilolite	High ion exchange potential and sorption capacity. Chemically stable. Low cost, readily available.
Steatite (only as a solid plug for small boreholes)	Low permeability. Good strength. Low cost.
Grouts Portland cements Hydrothermal cements	Low permeability. High adaptability. Low cost, readily available.
Concretes Portland cements plus aggregate Hydrothermal cements plus aggregate	Good strength. Low permeability. High adaptability. Low cost, readily available.

TABLE B-XXIII

MATERIALS SET ASIDE AT THIS TIME

Material	Reason for Setting Aside
Granite Natural glass Slate Serpentine Shale	Generally have the same properties as basalt in similar applications and would be less readily available.
Vermiculite	Same attributes as smectite clays but somewhat less readily available in comparison.
Kaolinite	Other clays have better ability to inhibit radionuclide migration. (Moderate ability to exchange anions in a solution--potential future application.)
Illite Talc	Generally excelled by other rocks and minerals in function classifications.
Gold Silver Platinum Copper Lead Metal alloys Carbon	Generally excelled by other materials in function classifications; also, very high cost and low availability for some.
Tar	Generally excelled by other materials in function classification.
Amber	Potentially unstable in the repository and plug environment.
Mullite	Similar to steatite but no ion exchange potential.

- Are adequate data available for each candidate plug material so that it can be usefully studied within the time frame of current pre-conceptual design studies and testing programs? (addressed in Step 4);
- What function or functions could each material perform in a plug? (addressed in Steps 1 and 3);
- How well would each material perform these functions? (addressed in Steps 5 and 6); and
- Taking into account the resource and contractual requirements of the pre-conceptual design studies and testing programs, as well as the relative abilities of each material to perform the various required plug functions, which materials should receive highest priority for inclusion in pre-conceptual design studies and testing programs? (addressed in Step 7).

The selection process handles these issues in a systematic manner and documents, in a quantitative form, answers to the five questions listed above. Any evaluation of this type requires the incorporation of professional judgment. However, the procedure attempts to reduce the effects of subjective judgment where possible. In addition, because the selection mechanism is systematically documented, another investigator can determine how differences in judgments would affect the final results of the selection process.

Finally, because the process is clearly defined and systematic, it is possible to evaluate any proposed plug materials that may come to light in the future on a basis that is consistent with the evaluation presented here.

In view of the large number of materials identified in Step 1 as being potentially applicable in plugs, the final list of selected materials may appear short. However, the length of this list is somewhat deceptive. Some of the items, such as smectite clays and concretes, are actually categories of materials that have a variety of specific types to be investigated. In addition, there are various additives (not discussed here) to be investigated for use with some of the materials. Finally, a mixed component plug could combine two or more of the materials on the list in various proportions.

With all of these many possible variations available for investigation, the list of selected materials provides an ample group of materials and mixtures with potential promise for preconceptual design and testing.

APPENDIX B

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APPENDIX C

DETAILED DATA FROM GEOCHEMICAL TESTING PROGRAM

APPENDIX C

DETAILED DATA FROM GEOCHEMICAL
TESTING PROGRAM

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TABLE C-I
SPECIMENS AND SAMPLE IDENTIFICATION NUMBERS
USED IN THE GEOCHEMICAL TESTING PROGRAM

<u>Sample ID No.^a</u>	<u>Composition</u>	<u>Proportions^b</u>	<u>Description^c</u>
1	Basalt		Single piece, polished face
2	Basalt		-10/+40 mesh
3	Basalt		
4	Basalt/Sand	1:1	
5	Basalt/Oregon bentonite	1:1	Bentonite -325 mesh
6	Basalt/Wyoming bentonite	1:1	Bentonite -325 mesh
7	Basalt/Shurgel	1:1	Shurgel -325 mesh (processed bentonite)
8	Basalt/Aquagel	1:1	Aquagel -325 mesh (processed bentonite)
9	Basalt/Ringold clay ^d	1:1	Clay -325 mesh
10	Basalt/sand/Oregon bentonite	1:1:1	Bentonite -325 mesh
11	Basalt/sand/Wyoming bentonite	1:1:1	Bentonite -325 mesh
12	Basalt/sand/Ringold clay	1:1:1	Clay -325 mesh
13	Basalt/zeolite/Oregon bentonite	1:1:1	Zeolite, bentonite -325 mesh
14	Basalt/zeolite/Wyoming bentonite	1:1:1	Zeolite, bentonite -325 mesh
15	Basalt/zeolite/Ringold clay	1:1:1	Zeolite, clay -325 mesh
16	Oregon bentonite		-325 mesh
17	Wyoming bentonite		-325 mesh
18	Oregon bentonite/sand	1:1	Bentonite -325 mesh
19	Wyoming bentonite/sand	1:1	Bentonite -325 mesh

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RHO-BWI-C-66

TABLE C-I (continued)

<u>Sample</u> <u>ID No.^a</u>	<u>Composition</u>	<u>Proportions^b</u>	<u>Description^c</u>
20	Oregon bentonite/zeolite	1:1	Both -325 mesh
21	Wyoming bentonite/zeolite	1:1	Both -325 mesh
22	Oregon zeolite		-325 mesh
23	Ringold clay		-325 mesh
24	Ringold clay/sand	1:1	Clay -325 mesh
25	Fondu/sand/basalt	1:1:1	Fondu = hydrothermal cement (brand name)
26	Secar/sand/basalt	1:1:1	Secar = hydrothermal cement (brand name)
27	(Portland pozzolan cement + sand)/basalt	1:1	
28	(Portland Type II cement + sand)/basalt	1:1	
29	(Portland Type V cement + sand)/basalt	1:1	
30	(Fondu + zeolite)/basalt	1:1	
31	(Portland pozzolan cement + zeolite)/basalt	1:1	
32	(Portland Type II cement + zeolite)/basalt	1:1	
33	(Portland Type V cement + zeolite)/basalt	1:1	
34	(Portland Type V cement + silica flour)/basalt	1:1	
35	Basalt core + concrete		Bulk specimen supplied by Rockwell

TABLE C-I (continued)

<u>Sample ID</u>	<u>No.^a</u>	<u>Composition</u>	<u>Proportions^b</u>	<u>Description^c</u>
36		(TXI Chem Com cement + Lassenite)/sand	1:1	TXI Chem Com = portland cement with shrinkage compensating agent (brand name); Lassenite = natural pozzolan additive (brand name)
37		(Portland Type V cement + silica flour + Plastiment)/sand	1:1	Plastiment = organic water reducing retarder agent (brand name)
38		(Portland pozzolan cement + silica flour)/sand	1:1	
39		(Portland Type V cement + Lassenite)/sand	1:1	

^aLetter designations shown with Sample ID numbers on the following tables are as follows: A, B, and C refer to 3-month, 2-month, and 1-month 250°C static tests, respectively; D, E, and F refer to 3-month, 2-month, and 1-month 150°C static tests, respectively

^bAll proportions are by weight to ±0.001g.

^cAll materials ground to -200 +325 mesh, unless specified otherwise.

^dRingold clay from Unit D (see Chapter 5, Section 5.3.4.).

TABLE C-II

RESULTS OF ATOMIC ABSORPTION ANALYSIS OF SOLUTIONS FROM
250°C STATIC TEST AFTER 1-MONTH EXPOSURE, IN MG/L

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
Ground Water ^a	26	10	1	<0.2	7	≤0.01	0.1
Autoclave Solution ^b	94	18	0.2	10	53	0.04	120
1C ^c	116	14	0.8	<0.2	14	4	180
2C	114	12	0.4	<0.2	6	0.6	180
3C	116	18	0.2	<0.2	6	≤0.01	60
4C	140	12	0.2	<0.2	14	2	80
5C	170	16	1.4	<0.2	74	14	140
6C	134	14	<0.01	<0.2	4	0.6	180
7C	146	12	<0.01	<0.2	2	1.2	220
8C	695	18	0.7	2	9	6	60
9C	164	12	<0.01	<0.2	6	0.8	280
10C	136	6	0.2	<0.2	50	1.2	120
11C	88	10	1	5	140	6	8
12C	108	8	<0.01	<0.2	12	0.8	40
13C	130	4	<0.01	<0.2	10	1.6	80
14C	112	10	0.2	<0.2	4	1.6	200
15C	106	4	0.01	<0.2	4	1.4	140
16C	17	2	0.2	<0.2	256	1	6
17C							
18C	174	14	0.2	<0.2	82	<0.01	100
19C	114	8	<0.01	<0.2	3	0.8	160
20C	2	<0.05	<0.01	<0.2	1	<0.01	14
21C	132	22	<0.01	<0.2	10	28	80
22C	112	18	0.2	8	6	8	140
23C	120	8	<0.01	<0.2	6	4	240
24C	142	6	<0.01	<0.2	14	0.2	40

^aAs prepared.

^bAfter 1 month.

^cLetter "C" denotes 1-month exposure 250°C static test.

TABLE C-II (continued)

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
25C	112	18	<0.01	<0.2	14	2	80
26C	110	16	<0.01	<0.2	10	0.6	120
27C	122	10	100	52	144	76	80
28C	382	40	1	6	84	2	80
29C	2	<0.05	<0.01	<0.2	1.4	0.2	80
30C	2	<0.05	<0.01	<0.2	<0.05	0.2	10
31C	2	<0.05	<0.01	<0.2	2	2	8
32C	216	88	<0.01	<0.2	10	0.2	100
33C	135	11	1.1	<0.2	177	2.1	64
34C	2	<0.05	<0.01	<0.2	2	0.6	40
36C	2	<0.05	<0.01	<0.2	1.2	<0.01	40
37C	190	60	<0.01	<0.2	14	1.0	160
38C	176	16	1.4	<0.2	226	1.6	120
39C	206	14	4	12	260	6	100

TABLE C-III

RESULTS OF ATOMIC ABSORPTION ANALYSIS OF SOLUTIONS FROM
250°C STATIC TEST AFTER 2-MONTH EXPOSURE, IN MG/L

<u>Sample</u> ^a	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
Autoclave Solution ^b	52	10	0.2	<0.2	6	1.2	100
1B ^c	120	8	0.4	<0.2	4	1.4	160
2B	314	6	0.4	<0.2	6	2	120
3B	360	14	1.6	<0.2	10	4	80
4B	92	6	0.8	<0.2	10	2	80
5B	146	8	14	32	124	240	100
6B	76	8	2.8	8	8	10	80
7B	92	10	0.6	<0.2	6	4	160
8B	116	12	4	12	8	2	100
9B	94	4	0.4	<0.2	3	<0.05	140
10B	360	6	2.6	<0.2	142	1.2	100
11B	94	4	2.2	4	8	4	120
12B	54	2	0.4	<0.2	4	<0.05	140
13B	174	20	0.8	<0.2	34	<0.05	80
14B	46	4	0.4	<0.2	2	<0.05	120
15B	252	64	18	4	38	134	160
16B	156	14	1.2	<0.2	242	4	20
17B	50	4	1.6	<0.2	6	2	100
18B	48	2	0.2	<0.2	4	<0.05	80
19B	96	6	2.4	8	6	1.4	40
20B	148	26	1.6	7	26	388	440
21B	102	8	0.2	<0.2	4	8	160
22B	52	2	0.2	<0.2	4	4	120
23B	82	2	0.4	<0.2	4	4	60
24B	46	2	0.2	<0.2	2	12	80
25B	44	6	0.2	<0.2	6	2	80

^aSee Table C-I for description of sample.

^bAfter 1 month.

^cLetter "B" denotes 2-month exposure 250°C static test.

TABLE C-III (continued)

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
26B	48	8	0.2	<0.2	4	<0.05	80
27B	54	4	<0.01	<0.2	8	<0.05	100
28B	58	2	0.2	<0.2	10	<0.05	80
29B	54	2	0.2	<0.2	10	1.6	80
30B	50	10	0.2	<0.2	6	1.4	80
31B	62	6	3	8	116	8	80
32B	42	2	0.2	<0.2	10	1	80
33B	52	2	0.2	<0.2	8	<0.05	100
34B	64	2	0.2	<0.2	8	<0.05	100
36B	42	2	0.2	<0.2	14	<0.05	120
37B	44	2	0.2	<0.2	12	4	100
38B	50	4	5	20	256	8	100
39B	82	4	0.2	<0.2	17	2	100

TABLE C-IV

RESULTS OF ATOMIC ABSORPTION ANALYSIS OF SOLUTIONS FROM
250°C STATIC TEST AFTER 3-MONTH EXPOSURE, IN MG/L

<u>Sample^a</u>	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
Autoclave Solution ^b	34	12	0.2	<0.2	6	2	40
1A ^c	96	8	<0.01	<0.2	2	2	240
2A	92	4	<0.01	<0.2	4	20	180
3A	80	12	0.2	<0.2	4	12	140
4A	108	10	0.4	<0.2	40	60	140
5A	592	52	2.2	<0.2	194	2	100
6A	102	8	1	6	2	6	180
7A	96	10	1.6	8	10	20	180
8A	102	16	0.8	4	2	14	240
9A	70	6	0.2	<0.2	2	2	140
10A	76	4	1.4	6	30	6	100
11A	104	8	0.8	4	4	28	140
12A	78	4	<0.01	<0.2	2	12	140
13A	130	34	0.4	<0.2	10	18	60
14A	138	18	0.4	<0.2	20	16	100
15A	44	6	0.2	<0.2	2	8	100
16A	780	64	2.6	<0.2	262	6	120
17A	120	6	0.8	4	2	18	160
18A	236	14	0.6	<0.2	154	38	120
19A	72	8	0.6	<0.2	4	28	60
20A	288	28	0.2	<0.2	46	12	120
21A	122	24	1	<0.2	44	12	100
22A	114	34	1.6	16	30	14	140
23A	60	8	0.2	4	<0.05	8	120
24A	74	4	0.2	<0.2	4	10	140
25A	84	16	0.2	<0.2	8	12	100

^aSee Table C-1 for description.

^bAfter 1 month.

^cLetter "A" denotes 3-month exposure 250°C static test.

TABLE C-IV (continued)

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
26A	68	18	0.4	<0.2	4	14	60
27A	48	4	<0.01	<0.2	10	6	100
28A	96	6	<0.01	<0.2	28	2	100
29A	60	4	<0.01	<0.2	14	2	120
30A	56	10	<0.01	<0.2	6	2	120
31A	58	4	<0.01	<0.2	12	2	100
32A	86	6	0.2	<0.2	22	<0.1	100
33A	86	6	<0.01	<0.2	26	<0.1	100
34A	80	6	0.2	<0.2	42	2	120
36A	46	6	0.6	<0.2	76	14	100
37A	50	2	0.2	<0.2	16	2	100
38A	76	4	<0.01	<0.2	20	4	100
39A	76	6	<0.01	<0.2	46	2	100

TABLE C-V

RESULTS OF ATOMIC ABSORPTION ANALYSIS OF SOLUTIONS REMOVED
WHEN THE A SERIES WAS REBOTTLED AFTER 2 MONTHS IN THE AUTOCLAVE

<u>Sample</u> ^a	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
3A	68	12	<0.01	b	4	2	220
8A	104	12	0.4	b	2	8	120
9A	86	6	0.4	b	4	4	120
11A	90	6	6.6	b	4	2	160
12A	76	2	2.8	b	4	1.4	200
14A	62	6	4	b	2	1.6	180
24A	82	2	0.2	b	4	1.0	160
28A	100	4	0.4	b	24	<0.05	120
29A	56	10	3.6	14	74	60	320
30A	60	4	0.8	6	20	4	220
31A	62	2	0.4	b	12	<0.05	180
32A	72	4	0.2	b	20	1.8	220
33A	72	4	0.4	b	28	<0.05	160
34A	78	4	32	b	30	4	180
39A	76	4	0.4	b	48	<0.05	140

^aSee Table C-I for description.

^b{Fe} <0.2 ppm

TABLE C-VI

RESULTS OF ATOMIC ABSORPTION ANALYSIS OF SOLUTIONS REMOVED
AFTER 1, 2, AND 3 MONTHS FROM THE 150°C STATIC TEST, IN MG/L

<u>Sample</u> ^a	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
1-Month Test							
12F	52	18	<0.01	b	12	5	80
13F	376	94	<0.01	b	48	<1	80
21F	326	54	0.6	b	48	<1	40
25F	30	52	0.58	20	48	40	60
27F	80	48	<0.01	b	26	<1	80
39F	86	42	0.4	b	22	3	80
2-Month Test							
12E	100	22	24	b	8	2	120
13E	176	62	0.6	b	22	<0.05	40
21E	706	140	1.0	b	64	1.8	180
25E	36	80	12	20	36	40	80
27E	108	72	0.4	b	16	<0.05	120
39E	112	66	0.6	b	18	1.6	200
3-Month Test							
12D	70	42	0.4	b	12	2	100
13D	416	150	0.4	b	56	2	300
21D	652	136	2	b	140	0.08	100
25D	50	26	0.4	b	10	0.3	8
27D	156	94	66	138	136	64	80
39D	140	88	0.4	b	14	8	100

^aSee Table C-I for description.

^b{Fe} <0.2 ppm.

TABLE C-VII

RESULTS OF ATOMIC ABSORPTION ANALYSIS OF SOLUTIONS FROM
STIRRED AND 34.5 MPa STATIC TESTS, IN MG/L

<u>Sample</u>	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>
<u>Stirred Vessel</u>							
[250°C, 4.6 MPa, 2 weeks]							
Basalt	154	56	72	142	140	228	320
Zeolite	1,640	1,008	34	42	456	736	540
Bentonite plus Zeolite	1,456	552	52	32	1,134	298	580
Basalt plus Bentonite	608	19	0.2	0.3	16	<2	6
<u>High Pressure Vessel</u>							
[250°C, 34.5 MPa, static, 2 weeks]							
Basalt	102	50	22	40	72	78	420
Zeolite	458	40	0.2	<0.2	12	100	320
Bentonite plus zeolite	608	72	1.8	<0.2	206	6	200
Basalt plus bentonite	925	40	<0.2	<0.2	3	0.4	30
Basalt plus zeolite plus bentonite	412	134	30	40	140	8	260

TABLE C-VIII

RESULTS OF X-RAY DIFFRACTION ANALYSIS OF SOLID SPECIMENS
FROM STATIC, 250°C TEST; SINGLE NATURAL MATERIALS

Qualitative Phase Analysis (Vol %), After Indicated Exposure

<u>Sample ID No.*</u>	<u>Starting Material</u>	<u>1-Month</u>	<u>2-Month</u>	<u>3-Month</u>
3	65L-30A-5M	59L-27A-4M -10Mt	59L-27A-4M -10Mt	55L-26A-4M -15Mt
16	75Mt-25Q	88Mt-12Q	75Mt-25Q	95Mt-5Q
17	75Mt-20Q-5U	80Mt-20Q	90Mt-10Q	60Mt-10Q-30X
23	65Mt-10I-25Q	59Mt-9I-22Q -10X	65Mt-10I-25Q	52Mt-8I-20Q -20X
22	90C-10U	100C	100C	100C

*See Table C-I for description.

NOTES: Q = Quartz (SiO_2); L = Labradorite ($\{\text{Ca,Na}\}\text{Si}_2\text{Al}_2\text{O}_8$);
A = Augite ($\{\text{Ca,Mg,Fe}\}\cdot\text{SiO}_2$); M = Magnetite (Fe_3O_4);
Mt = Montmorillonite; I = Illite; C = Clinoptilolite
($\{\text{Ca,Na,K}\}\text{Al}_2\text{Si}_7\text{O}_{18}\cdot 6\text{H}_2\text{O}$), X = Unknown phase giving
single large peak; U = Unidentified

TABLE C-IX

X-RAY DIFFRACTION ANALYSIS OF PHASE CHANGES IN SOLID
SPECIMENS FROM STATIC, 250°C TEST;
MIXTURES OF NATURAL MATERIALS

Sample ID No.*	Unreacted	Test Interval		
		1-Month	2-Month	3-Month
4		≈0.10% Mt appears in 1 to 3 month tests		
5				Mt peak broader
6				Mt peak broader
7				
8		Lg. U peak	U gone	
9				
10			High Mt	High Mt
11				
12				
13				More Mt
14				Less Z
15		Increasing crystallinity in Mt Phase		
18		Mt increases 1 to 3 months		Small Z
19		Unidentified major peak develops		
20		Unidentified major peak develops		
21				
24				

*See Table C-1 for description.

NOTES: Unless otherwise indicated, x-ray spectra are superpositions of those from original, unreacted single components. Mt = Montmorillonite, U = Unidentified peak, Z = Zeolite

TABLE C-X

X-RAY DIFFRACTION ANALYSIS OF PHASE CHANGES IN SOLID
SPECIMENS FROM STATIC, 250°C TEST; CEMENTITIOUS MIXTURES

Sample ID No.*	Unreacted	Test Interval		
		1-Month	2-Months	3-Months
25		Strong Mt increases 1 to 3 months		
26		Small Mt decreases 1 to 3 months		
27		Mt increases 1-3 months		
28		U		
29				
30		Small Z	Z disappears	
31		Mt increases 1 to 3 months		
32				
33		U		
34				
36		Mt increases 1 to 3 months		
37		U		
38				
39				

*See Table C-I for description.

NOTES: No entry means spectra unchanged from starting material.

Mt = Montmorillonite, U = Unidentified Phase,

Z = Zeolite

TABLE C-XI
 PERCENTAGES OF SOLID MATERIAL RECOVERED
 AFTER 250°C STATIC TESTS

<u>Sample ID Number^a</u>	<u>Recovered Sample Weight (percent)</u>		
	<u>1 Month</u>	<u>2 Months</u>	<u>3 Months</u>
1	95.2	93.6	94.5
2	91.0	91.9	89.8
3	94.2	94.7	93.3
4	95.2	94.8	95.1
5	86.9 (B) ^b	86.4	94.7
6	89.3	92.8 (B)	94.8
7	91.5	94.3	91.4
8	93.2	96.0	95.0
9	96.1	93.7	96.2
10	89.6 (B)	91.2	89.8
11	95.6	93.6	95.0
12	95.3	93.6	95.5
13	89.6	94.2	89.7
14	91.9	87.2	93.9
15	91.6	89.4	77.5
16	92.8	79.9	93.2 (B)
17	92.8 (B)	76.5 (B)	98.0 (B)
18	91.2	83.9	90.1
19	87.5 (B)	96.0	95.2 (B)
20	96.3	86.8 (B)	92.7
21	88.4	94.5	89.8 (B)
22	84.4	84.1	82.0
23	96.6	95.4	96.2
24	95.5	91.1	94.9
25	97.2	95.5 (B)	96.1 (B)
26	95.5	93.8	94.7
27	95.9	96.9	96.0

^aSee Table C-I for description.

^bB = broken bag.

TABLE C-XI (continued)

<u>Sample ID Number^a</u>	<u>Recovered Sample Weight (percent)</u>		
	<u>1 Month</u>	<u>2 Months</u>	<u>3 Months</u>
28	98.7	97.8	95.9
29	98.7	97.3	97.3
30	96.0	91.4	90.2
31	92.2	90.2	89.3
32	93.9	86.4	91.8
33	92.8	84.3	90.9
34	96.1	93.7	94.7
36	97.7	96.4 (B) ^b	94.7
37	99.1	93.6 (B)	93.2
38	96.8	93.0	95.4 (B)
39	96.1	95.3	94.3

^aSee Table C-I for description.

^bB = broken bag.

TABLE C-XII

FISHER PARTICLE SIZE ANALYSIS OF SOLID SPECIMENS FROM
 STATIC, 250°C TEST, AFTER INDICATED EXPOSURE

<u>Sample ID No.*</u>	<u>Starting Material Avg Dia (μm)</u>	<u>1-Month Avg Dia (μm)</u>	<u>2-Months Avg Dia (μm)</u>	<u>3-Months Avg Dia (μm)</u>
3	32.34	4.77	3.78	3.86
16	2.94	4.17	3.62	4.11
17	7.34	9.67	6.82	12.38
23	2.56	3.46	2.28	3.92
22	2.58	3.90	2.76	3.06
4	-	3.87	3.01	3.84
5	-	3.49	2.66	3.55
6	-	4.08	5.93	4.98
9	-	3.10	2.01	3.14
18	-	3.72	2.69	2.84
19	-	4.65	5.04	3.66
24	-	4.42	2.65	2.99
20	-	2.97	3.38	2.00
21	-	3.58	2.72	2.60
10	-	3.34	2.93	2.44
11	-	3.72	3.21	2.88
12	-	3.19	2.96	2.25
13	-	2.88	2.29	2.35
14	-	3.46	2.67	2.12
15	-	2.76	2.27	1.91
25	-	3.20	2.87	1.90
26	-	2.16	1.98	1.76
27	-	4.57	2.23	2.28
28	-	1.76	1.79	1.97

*See Table C-I for description.

TABLE C-XII (continued)

<u>Sample ID No.</u>	<u>Starting Material Avg. Dia (μm)</u>	<u>1 Month Avg Dia (μm)</u>	<u>2 Months Avg Dia (μm)</u>	<u>3 Months Avg Dia (μm)</u>
29	-	1.77	1.62	1.53
30	-	2.26	3.50	2.12
31	-	1.93	1.34	0.90
32	-	2.28	1.81	1.23
33	-	2.16	1.35	1.01
34	-	1.28	0.60	0.75
36	-	1.76	1.80	1.18
37	-	2.91	1.46	1.44
38	-	1.35	0.68	0.79
39	-	1.64	0.47	0.61

TABLE C-XIII

AVERAGE POROSITIES OF POWDER COMPACTS FROM STATIC
250°C TEST, AFTER INDICATED EXPOSURE

<u>Sample ID No.*</u>	<u>Starting Material Porosity (%)</u>	<u>1-Month Porosity (%)</u>	<u>2-Months Porosity (%)</u>	<u>3-Months Porosity (%)</u>
3	52.7	46.3	45.6	44.9
16	51.6	44.6	42.7	45.9
17	41.5	31.5	33.2	33.9
23	49.1	49.8	45.3	51.6
22	53.0	55.0	53.4	56.6
4	-	46.4	49.7	45.1
5	-	44.1	51.0	52.2
6	-	39.2	45.0	45.7
9	-	50.2	47.5	47.4
18	-	49.4	44.9	50.9
19	-	42.2	39.0	38.4
24	-	49.0	49.3	46.3
20	-	54.9	50.1	50.6
21	-	43.7	43.0	39.8
10	-	50.4	51.4	46.2
11	-	43.8	45.6	38.9
12	-	49.8	50.5	44.9
13	-	49.2	50.8	44.5
14	-	45.6	41.1	47.6
15	-	52.9	48.2	45.7
25	-	54.2	52.7	47.6
26	-	56.6	53.4	52.8
27	-	59.4	52.5	48.9
28	-	57.0	55.8	51.8

*See Table C-I for description.

TABLE C-XII (continued)

<u>Sample ID No.</u>	<u>Starting Material Avg. Dia (μm)</u>	<u>1 Month Avg Dia (μm)</u>	<u>2 Months Avg Dia (μm)</u>	<u>3 Months Avg Dia (μm)</u>
29	-	1.77	1.62	1.53
30	-	2.26	3.50	2.12
31	-	1.93	1.34	0.90
32	-	2.28	1.81	1.23
33	-	2.16	1.35	1.01
34	-	1.28	0.60	0.75
36	-	1.76	1.80	1.18
37	-	2.91	1.46	1.44
38	-	1.35	0.68	0.79
39	-	1.64	0.47	0.61

TABLE C-XIII

AVERAGE POROSITIES OF POWDER COMPACTS FROM STATIC
250°C TEST, AFTER INDICATED EXPOSURE

<u>Sample ID No.*</u>	<u>Starting Material Porosity (%)</u>	<u>1-Month Porosity (%)</u>	<u>2-Months Porosity (%)</u>	<u>3-Months Porosity (%)</u>
3	52.7	46.3	45.6	44.9
16	51.6	44.6	42.7	45.9
17	41.5	31.5	33.2	33.9
23	49.1	49.8	45.3	51.6
22	53.0	55.0	53.4	56.6
4	-	46.4	49.7	45.1
5	-	44.1	51.0	52.2
6	-	39.2	45.0	45.7
9	-	50.2	47.5	47.4
18	-	49.4	44.9	50.9
19	-	42.2	39.0	38.4
24	-	49.0	49.3	46.3
20	-	54.9	50.1	50.6
21	-	43.7	43.0	39.8
10	-	50.4	51.4	46.2
11	-	43.8	45.6	38.9
12	-	49.8	50.5	44.9
13	-	49.2	50.8	44.5
14	-	45.6	41.1	47.6
15	-	52.9	48.2	45.7
25	-	54.2	52.7	47.6
26	-	56.6	53.4	52.8
27	-	59.4	52.5	48.9
28	-	57.0	55.8	51.8

*See Table C-I for description.

TABLE C-XIII (continued)

<u>Sample ID No.</u>	<u>Starting Material Porosity (%)</u>	<u>1-Month Porosity (%)</u>	<u>2-Months Porosity (%)</u>	<u>3-Months Porosity (%)</u>
29	-	55.4	52.1	52.3
30	-	53.1	50.9	47.8
31	-	59.1	54.9	54.6
32	-	58.0	56.4	55.5
33	-	59.6	56.9	55.8
34	-	63.3	59.0	57.7
36	-	59.2	52.2	57.7
37	-	59.0	56.8	56.7
38	-	63.3	59.4	56.7
39	-	60.5	59.2	60.6