PNL-5134

2F

Cover Sheet for a Hanford Historical Document Released for Public Availability

Released 1992

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

Battelle

DISCLAIMER

This is a **historical document** that is being released for public availability. This was made from the best available copy. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** The views and opinions of authors expressed herein do not neccesarily state or reflect those of the United States Government or any agency thereof.

3 3679 00058 6158

PNL-5734

DEVELOPMENT OF A TECHNICAL APPROACH FOR ASSESSING ENVIRONMENTAL RELEASE AND MIGRATION CHARACTERISTICS OF HANFORD GROUT

R. J. Serne
R. L. Treat
R. O. Lokken

September 1985

A Hanford Historical Document Released for Public Availability

1.0 SUMMARY

A Transportable Grout Facility is being constructed at the Hanford Site to immobilize low-level liquid radioactive waste in grout. This report addresses the grout and sediment testing methodology that is being developed at PNL to support assessments of the long-term performance of the disposed grout. Sediment is the soil that surrounds and underlies the disposed grout. A goal of these efforts is to certify tests for application at Hanford. An assessment of the long-term risks posed by grout requires data on the ability of grout to resist leaching of wastes contained within the grout. Additionally, data are needed on the ability of the sediments to retard the mobility of any wastes released from grout. The effects of aging on the ability of grout to retain waste must also be understood. Aging of grout can reduce or enhance the ability of the grout to contain waste.

Credible predictive modeling of the fate of hazardous constituents in disposed grout for periods of up to 10,000 years would best be performed using comprehensive, coupled hydrologic and chemical reaction codes based on knowledge of the mechanisms that control waste release and mobility. It is not clear yet how soon such codes will be available or which types of waste disposal options they will apply to. In the interim we must be content with simpler and separate models that address individual reactions such as leaching and adsorption. One of these models, the Semi-Infinite Solid Diffusion Leach Model, is a popular release model used to describe the leaching of grouts and other cemented waste forms. Because others have found success in describing laboratory leach experiments with cemented waste forms using this leach model and because it appears likely to err on the conservative side for the Hanford application, we currently endorse the use of this model and its supporting experimental methodology for approximations of grout waste release rates.

At the present time it is believed that the leachate from Hanford grout will not change significantly in its chemical nature once the major chemical reactions at the waste-form sediment interface are completed. Also, the range of sediments at Hanford through which the leachate will travel probably will not exhibit widely varying adsorption properties. These sediments are gener-

ally alkaline sands and silts containing little organic matter and have low-to-medium cation exchange capacities. Their interaction with the expected leachates from the Hanford grout should not appreciably affect the composition of the major constituents of the leachates. Therefore, the constant Rd adsorption model should be a useful first approximation of the adsorption processes likely to control trace concentrations of waste radionuclides and hazardous inorganic chemicals that may leach into the groundwater. Because the Rd approach is empirical, it does not lend itself to the identification of transport-controlling mechanisms, a key need for gaining credibility in long-term performance assessments. Despite its limitations, the Rd concept is believed to be a practical and useful tool for quantifying the interaction of Hanford grout leachate with Hanford sediments and assessing the mobility of waste species.

Unlike waste-form leaching, the research of radionuclide adsorption does not have a programmatic focal point in which standardization of techniques and procedures is occurring. At present we recommend that several different types of adsorption experiments be performed, including batch and column tests. Both types of tests are needed to increase the probability that the deficiencies of each are addressed.

The separation of the complex chemical interactions of grout, sediment and groundwater into simple leaching and adsorption processes for ease of experimentation and modeling is under question. Few experimenters have performed combined tests involving the waste form, sediment and leaching solution though such a combination represents the actual disposal scheme for Hanford grout. Consequently, investigations have been initiated at PNL that are intended to lead to the development of test procedures and methods of data analysis for such three-component tests.

Until the controlling chemical processes are identified in the combined tests, detailed characterization of the starting materials (grout, sediment, and groundwater) and resulting products (leached grout, reacted sediment and leachate) is believed necessary. The combined tests should be used to evaluate the usefulness of the separate tests as well as to demonstrate the performance of disposed grout. Once controlling mechanisms are identified and

coupled conceptual models and codes are available, many of the separate leaching and adsorption tests and detailed characterization of materials can be abandoned.

Preliminary results of a combined test have been obtained and the test is continuing. In the test, a block of grout containing radioactive Hanford Facilities Waste (HFW) is supported on a layer of Hanford sediment inside a plexiglass cylinder (column). Additional sediment is packed around the grout block and fills the remaining void space at the top of the column. Hanford groundwater is pumped into the bottom of the column where it flows through the bottom layer of sediment, around the grout, and through the upper layer of sediment. The effluent is collected in a sealed container to minimize evaporation and loss or gain of CO_2. The effluent is analyzed for (a) Eh, pH, and alkalinity, (b) major cations and selected trace metals, (c) major anions, inorganic carbon and organic carbon, and (d) radionuclide content.

The data collected to date show that the effluent is buffered at a pH between 8.0 and 8.8, whereas the effluent from a companion experiment (grout only, no sediment) rose quickly to the 11-12 pH range. The combined test appears to show net precipitation in the test column, whereas the grout-only test is showing net dissolution. The nitrite concentration rapidly and substantially increased in the grout-only test effluent but has not been measurable in the combined test effluent. The grout-only test effluent contained about five times the level of dissolved organic carbon that the combined test effluents showed. To date, no measurable quantities of radionuclides are present in the effluents from the combined test. The activity of ^{137}Cs and ^{85}Sr in the effluents in the grout-only test rose rapidly to steady-state values. Because previous batch adsorption tests and a column adsorption test showed strong adsorption of these radionuclides, the radionuclide data to date are as expected.

As part of the Hanford Grout Technology Program, numerous two-component leach tests have been underway since January 1985. Two of these tests, the ANS 16.1 test and the static test, are also showing leachates with distinctly different chemistries. A key to the differences seems to be the supply of HCO_3^- or dissolved CO_2 in the system. Differences in pH were also observed.

The pH of the ANS 16.1 system stabilized at approximately 8.5 whereas the pH of the static system rose to 12.0. At the higher pH, calcium and magnesium apparently precipitated, probably as carbonate minerals. It seems quite likely that grouts disposed in Hanford sediments will react with the carbonate-rich groundwaters to form calcite and carbonate-rich solids similar to those found in ancient artifacts from Cyprus and Greece. Whether these reactions would form protective layers on the grout that impede leaching is uncertain. Additional study is needed to explain the differences in these leach tests as well as the differences in the combined and grout-only tests.

This report discusses numerous activites that will be performed in conjunction with the experiments just described. These activities include: 1) detailed mineralogic, radiochemical and total chemical characterization of the grout and sediment versus distance from the interface, 2) detailed analysis of solution data by equilibrium thermodynamic codes to identify possible solid phase solubility controls and 3) mathematical analyses of the combined test results by mass transport theory ("waste package") models described in existing literature.

Recommendations for future study include 1) additional development of combined tests under saturated and partially saturated conditions 2) an evaluation of whether CO_2 gas will be supplied to the disposed grout monolith at a rate that maintains CO_2 equilibrium conditions at the grout-sediment interface 3) development of methods to supply CO_2 at an adequate rate should CO_2 equilibrium prove to be a controlling factor and 4) testing of artificially aged grout for leaching properties. Until the mechanisms of leaching and the subsequent interactions with sediments are better understood, it is difficult to suggest a specific direction for the development of combined tests. It is our hope that the analyses yet to be performed on the separate leaching and adsorption tests and the combined test will provide knowledge on controlling mechanisms and shed light on what parameters should be considered as most important in designing experiments to provide the data upon which long-term performance assessments are based. In spite of the current lack of understanding of the interactions among grout, sediment, and groundwater, and considering that this effort was not started until January 1985, significant progress has been made toward the establishment of testing methodologies for assessing the long-term performance of Hanford grout.

TABLE OF CONTENTS

Page

1.0 SUMMARY ii

2.0 INTRODUCTION 1

3.0 DESCRIPTION OF TYPICAL HANFORD GROUT BURIAL SETTING 2

A. DISPOSAL SITE CHARACTERISTICS 2

A.1 Grout Monolith Design 2
A.2 Moisture Barrier Design 3
A.3 Groundwater Chemistry 3
A.4 Sediment Characteristics 4

B. PERFORMANCE ASSESSMENT NEEDS 4

B.1 Grout Data Needs 4
B.2 Sediment Data Needs 6

C. PROBABLE HYDROLOGIC AND CHEMICAL PROCESSES CONTROLLING LEACHATE GENERATION AND SUBSEQUENT MIGRATION 6

C.1 Reactions During Grout Hydration and Setting 7
C.2 Durability of Grout-Like Materials 7
C.3 Contaminant Leaching 8
C.4 Leachate-Sediment Interactions 10

4.0 SOLID WASTE LEACH TESTS 11

A. DESCRIPTION OF TESTS 11

B. CONCEPTUAL LEACH MODELS 14

B.1 Solubility-Controlled Release Model 14
B.2 Semi-Infinite Solid Diffusion Leach Models 15
B.3 Finite Solid Diffusion Leach Models 18
B.4 Mixed Hydrologic-Chemical Reaction Conceptual Leach Models 19

5.0 SEDIMENT ADSORPTION TESTS 20

A. DESCRIPTION OF TESTS 20

A.1 Static Methods 21
A.2 Dynamic Methods 21
A.3 Other Methods 23

TABLE OF CONTENTS (Continued)

Page

B. CONCEPTUAL ADSORPTION MODELS 23

B.1 Constant Rd Model 24
B.2 More Sophisticated Adsorption Models 26

6.0 FACTORS TO CONSIDER WHEN DESIGNING COMBINED LEACHATE - ADSORPTION TESTS 26

A. PRE-TEST CHARACTERIZATION AND SELECTION 27

B. POST-TEST CHARACTERIZATION 28

C. SIZE AND TIME CONSIDERATIONS 29

D. REDOX AND CO_2 GAS EQUILIBRIA 30

E. EXTRAPOLATION OF DATA TO LONG TIME PERIODS 31

7.0 DESCRIPTION OF FIRST COMBINED EXPERIMENT 35

A. COMBINED TEST CONFIGURATION 35

A.1 Radioactive Grout 35
A.2 Hanford Sediment 37
A.3 Hanford Groundwater 37
A.4 Column Description 37

B. EFFLUENT COLLECTION 40

C. RESULTS AND DISCUSSION 40

8.0 RECOMMENDATIONS 48

A. ADDITIONAL ANALYSES 48

B. ADDITIONAL EXPERIMENTS 49

REFERENCES REF-1

2.0 INTRODUCTION

A Department of Energy (DOE) program is currently under way to design and construct a facility at the Hanford site in Richland, Washington, that will be used to immobilize and dispose of low-level liquid radioactive wastes as a solidified grout. This program is funded through DOE and is being managed by Rockwell Hanford Operations (Rockwell), with technical support from Oak Ridge National Laboratory (ORNL) and Pacific Northwest Laboratory (PNL). The Transportable Grout Facility (TGF) is scheduled for production start-up in December 1987.

In the TGF, low-level liquid wastes will be mixed with blends of grout-forming solids (Portland cement, fly ash, and clays) to produce a slurry. This slurry will be pumped to near-surface disposal sites where the grout will harden and cure to form large solid monoliths of immobilized wastes. As part of the program to demonstrate the acceptability of grout as a final disposal method, risk assessment studies are being performed. These studies are designed to assess the risks of grout as a disposal method for protecting the long-term public health and safety.

An assessment of the long-term risks posed by grout requires data on the ability of grout to resist leaching of wastes contained within the grout. Additionally, data are needed on the ability of soil (sediment) surrounding the grout to retard the mobility of any wastes released from grout. Any change that may occur with time (up to 10,000 years) in the ability of grout to contain wastes and the ability of sediment to retard waste migration must also be factored into a credible risk assessment.

This report addresses the grout and sediment testing methodology that is being developed specifically for assessing the long-term performance of grout disposed at the Hanford site. A key element of this methodology is the use of samples of actual Hanford waste grout, sediment, and groundwater in the various tests under development. A goal of these efforts is to certify tests for application at Hanford.

3.0 DESCRIPTION OF TYPICAL HANFORD GROUT BURIAL SETTING

A. DISPOSAL SITE CHARACTERISTICS

The development of tests for assessing the long-term performance of grout should consider several factors, including the characteristics of the disposal site. Disposal site characteristics include the design of the disposal system and other characteristics of the waste disposal site, such as sediment and groundwater properties that may affect the performance of the disposal system. The rates at which groundwater contacts the grout surface and subsequently leaches waste from the grout are functions of not only the rates of precipitation and evapotranspiration at the Hanford site, but also of the dimensions of the grout monolith over which water must flow and the effectiveness of moisture barriers over the grout for preventing penetration of percolating groundwater. If the rate of water contact with grout is very low, the release of waste from grout may be limited by the solubility of the waste elements in groundwater. If the rate of contact is high, release will be controlled by dissolution or diffusion processes. The chemistry of the groundwater also may significantly affect the rate of leaching and how the integrity of grout changes over the long time period. Once waste is released from grout, the rate at which it travels through the ground is strongly dependent on the characteristics of the sediment. Thus, tests for measuring the performance of the grout disposal system should involve conditions that are as characteristic of the disposal site as practicable.

A.1 Grout Monolith Design

The dimensions of the grout monolith, which are an important factor for determining rates of release of wastes from grout, depend on the design of a grout disposal facility. Currently, two different disposal facilities designs are being considered. One is a plastic-lined trench that would be used to contain low-dose-rate grouts. The other is a buried steel vessel that would be used for high-dose-rate grouts. In the latter case, the soil cover over the vessel serves as radiation shielding. Specific details of the two disposal designs are given in Kaiser Engineers (1985).

Because water percolates through the sediment in an essentially vertical pathway, the amount of water that contacts the grout each year can be determined by multiplying the percolation (or recharge) rate by the plan area of the monolith in the trench or vessel. Since grout is essentially impermeable, water will flow across all surfaces of the grout. Therefore, the rate that water contacts grout can be determined by dividing the amount of new water that contacts the grout each year by the overall surface area of the monolith. Even for large monoliths the rate is small, suggesting that the solubility of some waste species may limit leachability of those species.

A.2 Moisture Barrier Design

Moisture barriers will be emplaced over grout monoliths to reduce rates of water infiltration and contact with grout. The Hanford moisture barrier concept employs a layer of fine sediment over a layer of coarse sediment. The fine sediment holds the water in its capillaries at a depth where it is available for evaporation and transpiration by plant roots. Some water will still reach the grout by diffusing laterally from the edge of the barrier, but at very low rates. Postulated leaks in the barrier may result in higher water contact rates on isolated surfaces of the grout monolith than would be expected when no barrier is used. Hence, a range of water contact rates needs to be considered when designing and evaluating grout tests.

A.3 Groundwater Chemistry

The chemistry of groundwater may affect the leach rates of wastes from grout. Calcium, silicon, carbonate, and other chemical species present in groundwater may react and/or precipitate in the water-accessible pores of grout, rendering it less permeable and less leachable. On the other hand, magnesium and sulfate may react deleteriously with the grout, causing it to soften and potentially become more leachable (Lea 1971). The use of representative groundwater in grout tests is, therefore, important for extrapolating the performance of grout to long time periods.

A.4 Sediment Characteristics

The properties of sediment beneath the grout disposal site will affect the rate at which wastes will migrate toward sources of drinking water as well as concentrations of wastes in the drinking water. Hanford sediments at the grout disposal site are expected to range in texture from a gravelly sand to a silty sand. Previous work has shown that various soil types exist in strata above the Hanford water table (Brown 1959; McHenry 1957; Heller, Gee and Meyers 1985; and Routson and Fecht 1979). Each of these soils has properties that determine the rate at which water may percolate through the soil and the extent to which waste species are sorbed onto soil.

B. PERFORMANCE ASSESSMENT NEEDS

Data on the grout disposal system are needed to assess the performance of the system in terms of hazards posed to man. The primary data needs relate to the ability of grout to minimize the release of wastes through leaching and the ability of soil to retard the mobility of any wastes released from grout.

B.1 Grout Data Needs

Data on grout are needed to show that grout and the grout disposal system conform to established safety criteria. Applicable criteria include:

- The amount of separated liquid on grout must be minimized. Separated liquid contains wastes that could be highly mobile in the soil if the liquid were allowed to leak through the plastic liner or steel vessel that contains the grout. Any separated liquid that forms will be removed and recycled through the grout process. Therefore, grout tests that address this issue are not needed.

- Heat generated within the grout monolith must not result in unsafe generation of gases. Heat generation is expected to result in a maximum temperature of ~ 78°C at the center of the grout casting

(Treat et al. 1985). This temperature will not result in the generation of steam or any significant release of other gases. Standard calorimetry tests are sufficient to address this issue.

- The grout must support its own weight and that of overlying protective barriers. If the grout is not sufficiently strong, it may be crushed. This could result in the extrusion of waste-bearing liquid from grout and an increase in grout surface area, thereby rendering the grout more leachable. Compressive strength tests show that grout to be several times stronger than necessary. Standard compressive strength tests appear adequate.

- The grout must be sufficiently impermeable to preclude a direct flow of water through grout. If the grout is permeable, leaching would occur at very high rates. Permeability tests at PNL have shown that pressures in excess of 110 psi are required to cause liquid to flow through HFW grout. This characteristic should be sufficient to prevent liquid drainage and percolation.

- The grout system must limit the release and migration of wastes as required to assure public safety. Tests that address this criterion must consider the release and migration of waste in the short term as well as in the long term. Thus, the effects of aging on the ability of grout to retain waste must be understood. Aging of grout (e.g., through continued hydration of cement, crystal growth, and chemical reaction with groundwater) can reduce or enhance the ability of the grout to contain waste. The rate at which waste is released from grout will depend not only on the ability of the grout itself to contain the waste, but, as previously discussed, on the rate at which percolating groundwater leaches waste from the surface of grout. If the groundwater flows very slowly across the surface of the grout, waste will become concentrated in the groundwater and sediment in contact with the grout. This process will serve to decrease the

waste concentration gradient through the grout which will reduce migration rates of waste from inside the grout to the grout surface.

Grout performance tests and data appear adequately developed except for those pertaining to the rate of release of waste from grout. The data are needed for assessing the long-term performance of the grout disposal system in terms of its ability to isolate radionuclides and hazardous chemicals from the environment and human contact.

B.2 Sediment Data Needs

Data are needed on the ability of sediment to retard the rate of migration of wastes leached from grout. The required data include those which affect the rate at which water can migrate toward sources of drinking water. These include particle size, hydraulic conductivity, and water retention data. Other data required relate to the ability of sediment to adsorb wastes from migrating groundwater. A typical measure of the adsorption capability of soil is the distribution coefficient, R_d. This property can be measured in both static and dynamic laboratory adsorption tests.

C. PROBABLE HYDROLOGIC AND CHEMICAL PROCESSES CONTROLLING LEACHATE GENERATION AND SUBSEQUENT MIGRATION

Hanford grouts are formed by mixing liquid waste with dry solids, including cement, fly ash, clay, and sometimes other additives. The cement acts as a binder while the fly ash is added as an economical extender and to improve the pumpability of the slurry. Additives such as clay are used as suspending agents and to adsorb or sequester specific contaminants. For each specific liquid waste type, a grout recipe will be developed and applied that optimizes the waste form's stability and long-term leaching characteristics. The wastes and solids used in the recipe may enter into reactions that control leachate generation and subsequent migration of waste.

C.1 Reactions During Grout Hydration and Setting

The dry Portland cement used in grout formulation is a mixture of tricalcium silicate ($3CaO \cdot SiO_2$), dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$), tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) and other constituents. Upon wetting, these minerals hydrate, forming polymeric chains of mostly amorphous calcium silicates, crystalline aluminoferrites and aluminates, and portlandite ($Ca(OH)_2$). When other components are present, such as sulfate in wastes or bicarbonates in the groundwater, other reactions occur, forming ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), calcite ($CaCO_3$) and carbonated calcium aluminates and ferrites.

Upon hydration and curing, the permeability of the grout decreases significantly. This serves to physically isolate waste salts from future water contact. Futhermore, some of the waste constituents chemically react with the grout minerals or additives and become more strongly bound in the grout matrix. Some of the pH-sensitive cations such as trace metals, actinides, etc., may form insoluble hydroxides in the high pH environment inside the grout. Certain clay additives adsorb cations such as cesium. Matsuzuru and Ito (1977) show that the addition of 10-20% by weight zeolite (a form of clay) to the dry grout ingredients can decrease the effective leach rate of cesium by two to three orders of magnitude. Thus, some waste constituents are sequestered in the grout by strong chemical bonds while other waste constituents are physically isolated in the small pores of the grout.

C.2 Durability of Grout-Like Materials

Roy and Langton (1982, 1983) studied ancient human artifacts constructed of materials similar to Portland cement and found these artifacts (water containers, aqueducts, etc.) to be relatively sound. Nearly 40 samples from Greece and Cyprus dating from 400 B.C. to 200 A.D. were extensively studied. Mineralogic, surface and bulk chemical analyses confirm that the cementitious materials have remained relatively intact for up to 3000 years in the presence of surface and subsurface waters. Many of the artifacts, such as aqueducts, bath basins, and drinking mugs, were used to contain water or were in contact with water nearly continuously over this length of time. Reaction products of

the kind previously discussed were identified (e.g., hydrated calcium aluminate and hydrated calcium ferrite crystals as well as calcite and carbonated calcium aluminates and ferrites). The presence of these reaction products attests to their durability and suggests that modern cementious materials will be durable as well.

C.3 Contaminant Leaching

Water percolating through Hanford sediments may leach wastes from the grout. The amount of percolating water that contacts a grout monolith in the normal Hanford shallow-land burial setting without a moisture barrier present is controlled largely by the amount of recharge in the overlying vadose sediments. Currently, the groundwater recharge rate at Hanford is not known with certainty, but for bounding calculations a value between 0.5 and 5.0 cm/year has been adopted for the Hanford Defense Waste Environmental Impact Statement (HDW-EIS).

Qualitative permeability tests conducted at PNL have shown that more than 110 lb/in^2 over-pressure is required to force water to flow through HFW grout. Thus, it seems reasonable that any recharge water that encounters the grout monoliths will advect around the grout. Some of the recharge water at the grout surface will diffuse into and out of the grout and react chemically, but will not advect through. Thus, a release model based on diffusion and chemical reaction processes seems appropriate.

For grouts containing radioactive and chemical hazardous wastes, the release of wastes is most often described as an effective diffusion process. Water diffuses into the grout and dissolves or desorbs wastes in the grout. Solubilized wastes then diffuse out of the grout into the surrounding sediments. In reality, the actual processes that control grout leaching are complex, but most of the available literature on grout and cement leaching argue fairly conclusively that an effective (or lumped) diffusion model explains the observed data satisfactorily. In water most cations and anions exhibit diffusion coefficient of approximately 10^{-5} cm^2/sec. Using the effective diffusion model, most radionuclides and, by inference, inorganic hazardous chemicals leaching from cementitious waste forms exhibit a wide

range of coefficients ranging from 10^{-6} to less than 10^{-12} cm^2/sec. The large range in the effective diffusion coefficients observed is a reflection of the other processes, such as adsorption, precipitation, and mineral substitution, that impede the release of some constituents.

The effective diffusion model is used because it is simple and yet satisfactorily describes most laboratory leaching data over the months to a few years for which data are available. More complicated models would require complete analysis of the chemical and mineralogical nature of the grout both before and after contact with leachant and a complete chemical characterization of the leachate solution versus time. Further, the grout and interstitial water probably vary with position relative to the grout surface such that bulk analyses of the grout solid after leaching and analyses the bulk solution do not accurately represent the actual leaching conditions. Microanalytical techniques that allow analyses at the surface of the grout and at various depths may be necessary to adequately describe all of the interactions. No experimenters on low-level nuclear waste-form leaching have attempted detailed analysis of the bulk solids and leachates, let alone the potentially numerous micro-environments.

While preliminary analyses reported in the HDW-EIS indicate that a protective barrier emplaced over disposed grout can effectively eliminate infiltration of water, moisture will still exist in the porous sediment surrounding the waste. Furthermore, while water is usually seen as a vehicle for transport (i.e., in advection and dispersion processes) it is also a conduit for transport (i.e., by diffusion). Therefore, a moisture barrier is assumed to eliminate the relatively rapid release and transport from grout waste forms caused by advective transport, but releases are still assumed to occur by diffusive transport through the virtually immobile soil water. In this scenario, it is assumed that the diffusive transport pathway controls the release and transport of wastes. The grout is assumed to supply radionuclide concentrations at maximum levels at the grout-sediment interface until the source is depleted. Driven by these maximum, constant concentrations, the diffusion-dominated water pathway conducts contaminants directly to the unconfined aquifer and laterally to the advection-dominated water transport

pathways outside the barrier's influence. A more realistic release and transport model should take into account the influence of the grout on release. For example, a leach rate can be defined for each individual element in the grout inventory. These release rates may drop off significantly with time as the outer surface of the grout is leached and releases must come from the mass or activity stored in the interior of the monolith.

Release from beneath a properly functioning moisture barrier is assumed to occur as a result of diffusive transport through the sediment pore water. This transport mechanism will apply if the barrier functions as designed. If the barrier fails, a coupled advection-diffusion transport model will be required to describe release and transport because both these processes may provide significant contributions to the overall release. Such a combined advection-diffusion transport model will require detailed hydrologic knowledge of the neighboring unsaturated sediments and an understanding of the mechanisms of release of contaminants from the grout surface.

C.4 Leachate-Sediment Interactions

After leachate from within the grout matrix diffuses to the surface of the monolith, it will enter the partially saturated sediments that surround the grout. Upon entering the sediments, the leached species can be advected away by percolating water or diffused away through the pore water contained in the partially saturated vadose sediments. By either pathway, the wastes will eventually reach the water table. In both the vadose sediments and saturated aquifer sediments, chemical reactions, such as adsorption and precipitation, and physical processes, such as diffusion and dispersion, will change the composition and concentration of the leachate. In the desert climate at Hanford, it is likely that the concentrations of many chemical constituents in solution at the grout-sediment interface will be at their maximum values. Also, after an initial stabilizing period, it is unlikely that redox and pH conditions will change dramatically as the leachate is transported away from the sediments surrounding the grout. From these two assumptions, it is inferred that any dissolution/precipitation reactions that might occur should

happen within and/or on the surface of the grout or in the sediment directly contacting the grout.

In this report, adsoption and sorption are surface processes in which radionuclides in solution become chemically fixed on the surface of grout or sediment. Sorption can significantly reduce rates of migration through sediments. Adsorption and sorption include processes other than ideal ion exchange, but exclude precipitation of identifiable mineral or amorphous compounds. To quantify adsorption, the distribution of the adsorbate between the solid phase (sediment) and the solution phase is measured. The resulting value or distribution coefficient is often labelled Kd, D, or Rd. Adsorption is further defined and discussed in Section 5.

4.0 SOLID WASTE LEACH TESTS

The certification of leach testing methodologies for nuclear waste forms has been a major endeavor of the Materials Characterization Center (MCC) since its inception. Numerous articles and workshop proceedings describe the theoretical and conceptual models and practical aspects of leaching. The interested reader should explore the available literature such as Dayal, Arora and Morcos 1983; Godbee, Anders and Neilson 1980; Moore, Godbee and Kibbey 1977; Sambell, Smitton and Elsden 1982; Mendel 1982; Machiels and Pescatore 1981; Claassen 1981; Richardson 1981; ANS 1984; and MCC 1985a and b. The latter three references discuss in great detail specific protocols (methodologies) for performing leach tests. Specific leach tests used to generate waste release data for nuclear waste forms such as grout and mathematical models used to describe the release are present in this section.

A. DESCRIPTION OF TESTS

There are three types of laboratory leach tests commonly used on solidified nuclear wastes: static, intermittent solution exchange, and once-through flow. The static leach test involves the simple leaching of a solid waste form in a set volume of leachant inside a closed container. The resulting leachate is sampled at set times and analyzed for contaminant concentra-

tions. In some cases, pH, Eh and other chemical constituents are also analyzed. Rarely are detailed characterizations of the solids performed at the end of the experiment to gain further insight into the leaching process.

The static leach test requires minimal space and equipment and is generally quite simple to perform. Interpretation, on the other hand, is not always straightforward. The measurement of leach rates should consider the potential for waste deposition on the container wall. Westsik et al. (1983) and Columbo (1983) describe experiments in which significant amounts (40 to 80%) of the actinides leached were found on container walls and not in solution.

Static leach tests can be used to generate data to fit a solubility-controlled conceptual model, although diffusion-controlled conceptual models also can be fitted from static experiments. These conceptual models will be briefly described in the following section. Standard methods for static leach tests of nuclear waste forms are described in great detail in MCC 1985a and b. Specific tests include "MCC-1P Static Leach Test Method," "MCC-2P Static, High Temperature Leach Test Method," and "MCC-3S Agitated Powder Leach Test Method." The latter test is used to speed up the leaching process by greatly increasing available surface area for leachant contact.

Intermittent solution exchange leach experiments use the same type of containers as static experiments, but periodically the waste form is placed in fresh leachant. This type of experiment is endorsed by the American Nuclear Society (ANS 1984) for leaching low-level cementitious or grout-like waste forms. The intermittent solution exchange test is used in place of a static test when leaching is controlled by diffusion. The conceptual mathematical model for diffusion-controlled leaching can be reduced to a very simple equation if the waste form-solution interface has essentially a zero concentration of waste constituents. This condition exists if the leachant is in contact with the waste form only briefly, resulting in leached material being swept away from the interface. Specific protocol on the frequency of solution exchange and the solid waste form surface area-to-solution volume ratio are found in ANS 1984. The method is facilitated by using two leach containers and supporting the solid waste form by string in the middle of the leaching

solution. The solid sample can be transferred from one container and placed in a companion container prefilled with fresh leachant at the designated times. After leachate sampling, the used container may be rinsed or cleaned to evaluate the level of waste deposition on the container wall and then readied for re-use. The use of crushed or powdered waste forms is not easily accommodated using the ANS procedure.

The final type of leach test is the once-through flow test in which a waste form is packed or suspended in a column and leachant is slowly percolated over the waste form. Effluent solution is collected downstream from the waste form. Details on one type of once-through flow leach test are found in MCC-4S, "Low-Flow-Rate Leach Test Method (MCC 1985b)." This method is based on work performed at Lawrence Livermore National Laboratory (Coles et al. 1978; Weed and Jackson 1979; and Coles 1981). The MCC does not recommend that this test method be used on crushed or fine-grained waste forms. The lowest flow rate possible with the pump recommended in the protocol is 0.001 ml/min (525.6 ml/year). For a 1000-ml leach container with a 5.4-cm radius and 10.8-cm length, this volumetric flow rate equates to a linear flow rate of 5.7 cm/year. When a waste form is present in the leach column, it will reduce the cross-sectional area across which flow can occur and the linear flow rate will be higher. For instance, if a 0.5-liter right cylinder of grout were placed in a one-liter leach column, the linear flow rate would increase to 15.4 cm/year assuming the grout aspect ratio, length/radius, equals 2. As the current groundwater recharge rate at Hanford is assumed to be 0.5 cm/year, even the slowest possible leach flow rate by this test is high by about an order of magnitude. However, because the grout is essentially impermeable to the advective flow of water, water will flow over the surface of grout at a higher velocity than it would otherwise travel in the sediment.

A key assumption of the MCC-4S leach test is that the rate of plate-out of wastes on the column wall occurs uniformly during the test. Corrected leach rate calculations must await the end of the experiment when the column and effluent collection tubing can be stripped of any plate-out material.

Another flow test sometimes used is MCC-5S, "Soxhlet Leach Test Method," (MCC 1985b). In this test, a waste form specimen is suspended in an apparatus

in which condensing water trickles over the specimen and overflows into a boiling reservoir. The boiling reservoir collects dissolved elements and supplies steam to the condenser which generates the water that trickles over the waste form. In essence, the system is a recirculating leach test in which fresh condensate continually flows over the waste form. Such a test is an unrealistically harsh leach test in that the leachant, hot distilled water, is quite corrosive and causes accelerated leaching.

B. CONCEPTUAL LEACH MODELS

As mentioned previously, intermittent solution exchange tests are endorsed by the American Nuclear Society because the results can readily be interpreted by a diffusion model. The semi-infinite solid diffusion leach model is one of the models described in this section that are used to interpret leach rate data. The other models are the solubility-controlled release model, finite solid diffusion leach models, and mixed hydrologic-chemical reaction conceptual leach models.

B.1 Solubility-Controlled Release Model

If the laboratory data show that a constant or steady-state concentration is rapidly established in the leachate, it can be speculated that a solid phase within the grout or a reaction product at the grout surface is limiting the solution concentration. Predictions of release over the long-term can then be obtained assuming that the concentration in the leachate remains constant until the controlling material is exhausted. This constant concentration model is the simplest of the solubility-controlled release models. The solubility of any solid is defined by the product of the thermodynamic activity of each of the species formed upon dissolution. For example, if the release of ^{90}Sr and ^{60}Co from the waste grout happened to be controlled by the solubility of $SrCO_3$ and $Co(OH)_2$ solids, then the products $[Sr^{+2}][CO_3^{-2}]$ and $[Co^{+2}][OH^-]^2$ would remain constant during dissolution ([ ] denotes thermodynamic activity which can be related to concentration). If the pH of the leachate changes, both $[OH^-]$ and $[CO_3^{-2}]$ would likely change and thus the $[Sr^{+2}]$ and $[Co^{+2}]$ would also change to maintain a constant solubility

product. Thus, additional information, particularly the effects of pH changes, must be considered when applying solubility-controlled release models. That is, concentration can vary even though solubility is being controlled by a solid phase.

To manage all of the ancilliary information and calculate the resulting solubility-controlled concentrations (which, as mentioned, can vary), a thermodynamic equilibrium code is often used. Examples of how to use such codes are found in Deutsch, Jenne and Krupka 1982; Strachan, Krupka and Grambow 1984; and Peterson et al. 1984. These codes may be used to evaluate whether certain solids could be controlling the concentrations of species in various leachants. Peterson et al. (1984) show how such codes can be used to estimate solution concentrations that should result when a liquid waste equilibrates with a sediment. The approach requires specifying precipitation and dissolution reactions. The leaching of Hanford grout can be evaluated using the same principles, and such data analysis is planned in FY-1986 using data from ongoing tests.

B.2 Semi-Infinite Solid Diffusion Leach Models

This type of diffusion model is the most popular release model used to describe the leaching of grouts and other cemented waste forms. This model is used by researchers at Brookhaven National Laboratory (Kalb and Columbo 1984; Arora and Dayal 1984; Dayal, Schweitzer and Davis 1984; Dayal, Arora and Morcos 1983), at Oak Ridge National Laboratory (Moore, Godbee and Kibbey 1977; Godbee et al. 1980; Clark 1977), at the Japan Atomic Energy Research Institute (Matsuzuru and Moriyama 1982; Moriyama, Dojiri and Matsuzuru 1977), and at the United Kingdom Atomic Energy Authority, Harwell (Sambell, Smitton and Elsden 1982). It is used to analyze laboratory leach data on cylindrical blocks of cemented or grout waste forms in which nuclear wastes are incorporated. This model is endorsed by the American Nuclear Society and is the basis for their recommended leach test ANS-16.1, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes," (ANS 1984). The theoretical equations for diffusion-controlled leaching that follow are based on the following ideal conditions:

1. Once leaching commences, the concentration of the species being leached is zero in the solution at the waste form surface. In other words, dissolved waste is swept away from the surface as soon as it diffuses out of the waste form.

2. The leachant solution is continually moving past the waste form and its composition never changes significantly.

3. The solid waste form is homogeneous and remains essentially unchanged chemically and physically during the leach process. In other words no significant chemical alterations occur and the mass of constituents removed from the waste form is negligible in comparison to the total mass in the waste form. This is known as the semi-infinite requirement.

4. The surface is smooth and does not deteriorate with time or acquire a protective layer (i.e., the surface area is constant and equal to the geometric surface area).

5. There are no time-dependent interactions among the leachable species, the leachant, and the solid matrix.

6. The radionuclides and hazardous chemicals of interest are present as single chemical species.

7. The leachable species are mobilized by the leachant such that bulk diffusion is the limiting process.

Although the semi-infinite solid diffusion leach model is based on seven simplifying assumptions, it has found acceptance among many researchers. It is used to interpret laboratory leach tests on cemented waste forms and grouts in which the leachant is either changed periodically or contacts the solid in a once-through flow apparatus.

The mathematical description of a diffusion model that meets the above assumptions yields a diffusion coefficient for each leached species. The effective diffusion coefficient lumps all of the chemical and physical interactions that may actually be occurring into a single value that defines release rate.

There are two mathematical descriptions of this model commonly used to analyze laboratory data based on the leaching of semi-infinite solids.

$$D_e = \frac{\pi}{4} \left(\frac{\sum_{n=1}^{N} a_n}{A_o} \right)^2 \left(\frac{V}{S} \right)^2 \frac{1}{t}$$

$$D_e = \pi \left(\frac{a_n}{A_o} \right)^2 \left(\frac{V}{S} \right)^2 \left(\frac{t - \frac{1}{2}(\Delta t)_n}{(\Delta t)_n^2} \right)$$

where D_e = effective diffusion coefficient

a_n = amount of species of interest leached during each leach interval

A_o = total amount of species in solid waste form

V = volume of solid waste form

S = surface area of waste form

t = total elapsed time since start of leaching

Δt_n = time duration of interval n

N = number of time intervals

The former equation is used to calculate the cumulative diffusion coefficient for species i and the latter equation is used to calculate the instantaneous or incremental diffusion coefficient for species i at leach interval n. If the leach experiments satisfy the seven conditions previously mentioned, both equations will give the same effective diffusion coefficient at all times.

Hanford grouts will be surrounded by sediment partially saturated with water. The water flow rate in the sediments around the grout monoliths is expected to be fast relative to the diffusion rate of water through the grout. However, it is doubtful that the flow rate of water around grout is fast enough to meet the first assumption, i.e., that dissolved waste diffusing out of the grout will be swept away from the surface and satisfy the boundary condition, concentration = 0 at t > 0. If the assumption is made that leached waste is swept away, the results of using this model will overpredict the release of species of interest if the leachate is not swept away.

Over a 10,000 year time frame, the mass removed from the grout could begin to deplete the original waste inventory such that the third assumption, the semi-infinite requirement, is not met. Here again, it can be shown that a semi-infinite solid would lead to higher calculated releases than would a finite solid. ANS 16.1 gives correction tables for various geometries to correct predicted release rates if the semi-infinite criterion is violated.

It seems quite likely that grouts disposed in Hanford sediments will react with the carbonate-rich groundwaters to form calcite and carbonate-rich solids similar to those found in the artifacts from Cyprus and Greece (Roy and Langton 1982, 1983). Whether these reactions would form protective layers on the grout that impede diffusion is uncertain. It does appear that chemical reactions such as this might further lower the release of certain species such as ^{90}Sr over long periods of time. Therefore, ignoring such chemical reactions may lead to further conservatism in release predictions.

Three other models for release by a semi-infinite medium include the effects of 1) concentration-dependent dissolution, 2) surface dissolution represented by a moving boundary, and 3) time-dependent, first-order dissolution. Mathematical expressions for the cumulative fraction leached, $\Sigma a_n/A_o$, by these three models can be found in Moore, Godbee and Kibbey 1977.

B.3 Finite Solid Diffusion Leach Models

The previously described models assume that the solid is very large and that the mass leached is negligible compared to the mass available. Moriyama

et al. (1975) and Nestor (1980) give mathematical expressions for certain geometric shapes for release from finite objects. Exact solutions for finite spheres and parallelpipeds are also available. To ascertain whether more accurate results could be obtained using finite solid corrections, a useful rule of thumb is that corrections become important only if more than 20% of the total mass of a constituent of interest has leached from the waste form. A second check is to test whether $D_e t^{1/2}$ is much less than r, the characteristic length parameter for a solid shape. If so over the time frame of interest, then it is safe to use the semi-infinite model equations.

B.4 Mixed Hydrologic-Chemical Reaction Conceptual Leach Models

Much discussion and preliminary basic research is ongoing within the nuclear and hazardous waste community in the area of coupling sophisticated water movement (hydrologic) codes with sophisticated geochemical (chemical reaction) codes. It is difficult at this time to predict when and if such coupling exercises will mature to the point that (1) practical experiments can be performed to gather necessary input data and (2) cost-effective predictions can be performed to estimate the long-term release of potentially hazardous wastes from solid waste forms in contact with water. Most of the funding and activity for this coupling activity has originated in high-level nuclear waste geologic disposal projects throughout the world. The coupling topic has been the focus of special symposia in the last few years (Muller, Langmuir and Neretnieks 1984; Muller, Langmuir and Duda 1983; and Tsang and Mangold 1984). No clear consensus is available as yet as to how soon or for what types of waste disposal options such detailed, mechanistically based coupled models will be available. Performance assessment models currently used for predicting long-term release from solidified low-level grouts and cemented waste forms have not advanced beyond the semi-infinite solid effective diffusion model described in Section 4.B.2. Most performance assessment predictions performed in the HDW-EIS and for HFW grout have relied on even simpler models such as the constant concentration solubility control model and a constant rate of release model.

dynamic methods. Static methods use a fixed mass of sediment or rock in contact with a fixed volume of water in a closed container. Dynamic methods use a fixed column of sediment and flow water through the column normally on a once-through basis. Adsorption test methods are described in the ensuing paragraphs.

A.1 Static Methods

The most commonly chosen static laboratory method used to evaluate nuclide sorption is the batch test, which involves contacting an adsorbent (disaggregated rocks or sediments, etc.) with an adsorbate (waste dissolved in groundwater). Except when higher temperature and pressure are used, the system is continuously agitated to ensure adequate contact. At specified times the solid and solution are separated and the resulting distribution of adsorbate between the solution and solid is determined. Because the equipment, space, cost, and time requirements are low and the methodology is quite simple, the batch method is popular. However, certain variables may affect results. These include: 1) method of tracer addition to solution, 2) solution-to-sediment ratio, 3) initial tracer concentration in influent solution, 4) particle size distribution, 5) method of separating solid and solution, 6) container material, and 7) temperature.

One significant limitation is inherent in the batch methodology, i.e., the typical analytical procedure for counting total radioactivity in solution and in the solid does not differentiate between multiple chemical species if they are present. Thus, the calculational scheme to generate distribution coefficients from total activities cannot separate the distinct sorption values for different species. For this reason, when there is any suspicion that multiple species with significantly differing distribution coefficients may be present, a different sorption test, such as a once-through-flow column sorption experiment, should be run to search for early breakthrough of one of the species.

A.2 Dynamic Methods

Once-through-flow column sorption experiments are the most frequently used of various dynamic adsorption tests. The classical use of once-through-flow column sorption testing involves permeable sediments and soils. The method has been used for many years to verify Rd values determined by batch methods (Routson and Serne 1972). Once-through-flow column experiments are versatile in that hydrodynamic effects (dispersion, colloidal transport, etc.) as well as chemical phenomena (multiple species, reversibility, etc.) can be studied.

Typical equipment used in dynamic column experiments includes a cylindrical container for the sediment, a pump to control the solution flow rate, an automatic fraction collector for obtaining effluent aliquots, and connecting tubing. For very slow flow situations, tests are often conducted in a controlled atmosphere-humidity chamber to minimize effluent evaporation. The experimental methodology for disaggregated or porous materials, such as sediments, is well developed (Serne et al. 1974; Nielson and Biggar 1961; Passioura and Rose 1971; Van Genuchten, Wierenga and O'Conner 1977).

Two practical constraints of dynamic adsorption testing are the amount of time available for experimentation and the frequency of equipment failure. The flow of water through low-moisture-content, partially saturated sediments is extremely slow. This slow flow, coupled with the retardation most radionuclides encounter, creates breakthrough times often exceeding a few years for columns only tens of centimeters long. Furthermore, failure of equipment, especially pumps and fraction collectors, places practical constraints on laboratory experimentation.

Another complication in using column data has been the difficulty of interpreting asymmetric or peakless break-through curves. When ideal chromatographic peaks are observed in column tests of porous media, Rd can be calculated. Otherwise, Rf, a nuclide retardation factor (ratio of the travel time of the radionuclide to the travel time of the carrier groundwater), can be directly evaluated by use of well-established equations (Burkholder et al. 1979; Inoue and Kaufman 1963; Harada et al. 1980). Several solutions also exist which can describe slightly asymmetric breakthrough peaks, e.g., those

discussed by Van Genuchten (1974); Pigford et al. (1981); Gee and Campbell (1980); and Gee et al. (1981), but there appears to be no mathematical method capable of yielding Rd or Rf values for these types of data.

A.3 Other Methods

Studies of two other laboratory methods, axial filtration and channel chromatography, have apparently been discontinued by most experimentalists because the first requires specialized equipment and the second, complex data reduction techniques. Meyer et al. (1978, 1981); Meyer (1979); Triolo (1979); Francis et al. (1978, 1979); and Brandstetter et al. (1979) describe these methods and discuss their strengths and weaknesses.

Recently a recirculating-column technique (Daniels et al. 1981) was used to investigate whether agitation, which may cause particle attrition and increased surface area in batch systems, is the cause of slow increases in Rd with time and larger Rd values than in comparable column experiments. The recirculating-column technique involves a closed system like the batch test but relies on recirculating flow to provide solution-sediment contact. The sediments are fixed in the column so that particle abrasion is minimized. A reservoir of solution is used to adjust the solution-to-solid ratio to equal that used in comparable batch tests. Contact time can also be adjusted to equal that in a batch test. At present, too few results are available to determine whether the recirculating-column method offers advantages over the batch and once-through-flow methods.

B. CONCEPTUAL ADSORPTION MODELS

In this report, the distribution coefficient is called Rd and simply refers to the ratio of mass or activity of a radionuclide present in the solid phase (rock or sediment) to the mass or activity present in solution (groundwater). This empirical ratio does not require equilibrium conditions, quantitative reversibility, or ion exchange as the governing process (Serne and Relyea 1983).

Several reports have recently questioned the usefulness of the distribution coefficient approach (Reardon 1981; Moody 1981; Coles and Ramspott 1982;

Muller, Langmuir and Duda 1983). As discussed in the following paragraphs, distribution coefficients are a complex function of the chemical and physical parameters of the systems being studied. Their dependence on a large number of variables causes problems in overall system performance models because at this time these models can use only a single value for the distribution coefficient and cannot easily account for change in the environment from the waste form to the biosphere. Experimenters are critical of the use of Rds because the values measured are specific to the laboratory system studied and do not necessarily represent the contaminant behavior in the burial environment. Despite these criticisms, existing safety assessments continue to rely on the distribution coefficient to model radionuclide adsorption. Serne and Relyea (1983) review the use of distribution coefficients and discuss their strengths and weaknesses for nuclear waste disposal applications. At the present time, the Rd concept is believed to be a practical and useful tool for quantifying the subsequent interaction of Hanford grout leachate with Hanford sediments. The approach is empirical, however, and does not lend itself to the identification of transport-controlling mechanisms. But, with care and adequate characterization of the leachate-sediment system, most of the currently identified problems can be minimized. The following paragraphs describe the Rd concept and its application.

B.1 Constant Rd Model

In this model, the distribution of the contaminant of interest between the sediment and solution is assumed to be a constant value. The distribution is assumed to be independent of the characteristics of the sediment, groundwater, and radionuclide and chemical concentrations. Typically, the distribution coefficient, Rd, for a given contaminant is determined in the laboratory using actual sediment from the study area and actual or simulated groundwater to which a radionuclide tracer has been added. The Rd value is defined as:

$$Rd = \frac{\text{amount of radionuclide adsorbed on solids per gm}}{\text{amount of radionuclide in solution per ml}}$$

The mass or activity present in the sediment and the solution must be sufficient to facilitate a quantitative determination. The experiments are often preceded by contacting the sediment with several aliquots of water before adding the radiotracer to approximate the conditions expected in the field.

Most of the laboratory studies performed to measure the distribution coefficients for radionuclides do not systematically investigate the effect of important parameters and do not attempt to identify the processes causing the observed adsorption. Because it is an empirical measurement, the Rd value does not necessarily denote an equilibrium value or require some of the other assumptions inherent in the more rigorous use of the term Kd. The Rd term is regarded as simply the observed distribution ratio of waste species between the solid and solution. The term Kd is reserved for true equilibrium reactions that show reversibility and which do not yield a distribution ratio that is dependent on the tracer concentration in solution.

The Rd approach, which depends upon experimental determination of Rd is quite simple, but is also limited in that it does not address sensitivity to changing conditions. If the groundwater properties change (e.g., pH, dissolved solids content), a new experiment must be performed. There is little incentive to characterize or measure in detail the basic chemical and physical parameters of the sediment and groundwater, because with this model, no dependency is explicitly accommodated. On the other hand, experimenters and modelers soon realize that the need to perform a new experiment to collect the Rd value for a different condition becomes burdensome and uneconomical. For this reason and to identify the mechanisms/processes that control adsorption, sorption experimenters often characterize their experimental systems by measuring selected parameters. Unfortunately, with no physical model, the experimenter has little guidance as to which parameters are important and worthy of measurement.

At the present time we feel that the leachate from Hanford grout will not change dramatically in its chemical nature once the major chemical reactions at the waste-form sediment interface are completed. Also, the range of sediments from the vadose zone through the unconfined aquifer at Hanford probably

will not exhibit widely varying adsorption properties. The sediments are generally alkaline sands and silts containing little organic matter and having low-to-medium cation exchange capacities. Their interaction with the expected leachates from the Hanford grout should not appreciably affect the major constituents of the leachates. Therefore, the constant Rd adsorption model should be a useful first approximation of the adsorption processes that are likely to control trace concentrations of waste radionuclides and hazardous inorganic chemicals.

8.2 More Sophisticated Adsorption Models

More sophisticated models, such as the adsorption isotherm, empirical parametric models, mass action models and electrostatic interactions models have been used to describe adsorption processes. Details can be found in Serne and Relyea 1983 and NEA 1983. At present, these models do not appear to have a useful application in this work and, hence, will not be discussed further.

6.0 FACTORS TO CONSIDER WHEN DESIGNING COMBINED LEACHATE - ADSORPTION TESTS

In Section 3, information required to evaluate the long-term hazards posed to man by disposed grout was identified. The two key parameters identified for this evaluation include the release rate of waste constituents from the solid grout and the ability of sediment to retard the rate of migration of wastes leached from grout.

The Hanford grouts will be disposed in shallow excavations in the partially saturated sediments of the Hanford site. Presently there is little information available on experiments in which solidified waste forms are placed in contact with sediments and then leached by representative leachants (e.g., groundwater). Typically the leaching process and subsequent interaction of leachate with sediment are studied separately in leach tests (waste form and water) as described in Section 4 and adsorption tests (leachate and sediments) as described in Section 5.

Recently questions have been raised about the possible effects of combined waste form, groundwater and sediment interactions and the effects of unsaturated hydrologic conditions on the release and transport of wastes from the waste form. Separate leach tests and adsorption tests ignore possible synergistic and antagonistic reactions. Typically these separate tests have been performed under saturated hydrologic conditions in which dissolved gaseous species such as CO_2 may become depleted, thereby changing the chemistry of the leachant. Because few experimenters have performed combined tests (waste form + sediment + leaching solution) and because such a combination represents the actual disposal scheme for Hanford grout, investigations have been initiated and are planned to lead to the development of procedures and methods of data analysis for combined tests.

Until the controlling chemical processes are identified in this three-component system, detailed characterization of the starting materials (grout, sediment, and groundwater) and resulting products (leached grout, reacted sediment and leachate) is believed necessary. After the controlling processes are identified, the level of characterization required can probably be reduced.

A. PRE-TEST CHARACTERIZATION AND SELECTION

In order to begin to understand the mechanisms that control the release of waste constituents from grout, it is recommended that the composition of the grout be determined. This will facilitate mass balance tracking of the various components of grout and may aid in identifying potentially important processes that affect release rates. The liquid waste streams that will be grouted should be characterized for pH, redox state, major cations, major anions and potentially hazardous trace constituents (i.e., the trace metals and inorganic ions regulated by State of Washington and the Environmental Protection Agency). The radionuclide content, isotopic content and organic content of the liquid waste should also be determined. If the organic content is significant, additional characterization, such as class of compound (e.g., acid, halogenated hydrocarbon, chelating agent, etc.) shnuld be performed.

In a similar fashion, a total chemical analysis of the solids used in the grout formulation (i.e., major oxides, trace oxides, carbonate, sulfate, halogen and organic content and mineralogic identification) should be performed. After mixing and curing the grouts, any separated liquid on the surface of the grout should be collected and analyzed like the liquid waste. The solid grout should be characterized in a manner similar to the solids used in the grout formulation, but including a radionuclide analysis and measurement of weight and dimensions. The grout should also be characterized by the leach tests discussed in Section 4.

The sediment should be characterized using the same techniques used for the grout and grout solids. In addition, particle size, surface area, and total cation and anion exchange capacity of the sediment should be determined. Specific adsorption coefficients (Rd) for important radionuclides and hazardous chemical species should be measured by the methods discussed in Section 5. The leachant, Hanford groundwater in this case, should be characterized in a manner similar to the liquid waste streams, but excluding the radionuclide analysis. As the waste release and transport mechanisms involving grout, sediment and groundwater become better understood, many of these analyses may be found unnecessary.

B. POST-TEST CHARACTERIZATION

At the conclusion of the laboratory tests, the grout should be recharacterized as before. A dissection of grout from the surface inward followed by the same total chemical, radionuclide and mineralogical characterization as a function of depth will aid in identifying the depth of changes, reaction products and, potentially, grout alteration mechanisms.

The sediment should also be analyzed as before with the addition of a radiochemical analysis. These analyses should be performed on samples selected from sediment in contact with the grout and sediments progressively downstream from the grout.

The leachate from the separate leach and adsorption tests and the combined test should be sampled versus time. In addition to measuring pH and Eh, a complete chemical and radionuclide analyses of the leachate should be per-

formed. The leachates should be filtered and preserved appropriately if analyses cannot be performed immediately. The effluent filters should be checked for visual signs of particles and analyzed for radionuclide content. If significant quantities of particles are observed, the particles should be totally characterized. Again, some of these analyses may be found unnecessary once an understanding of the controlling processes is gained.

C. SIZE AND TIME CONSIDERATIONS

Practical limitations exist on the amounts of material that can be tested and the time available for conducting the tests. In this section test size and time considerations with respect to the experiments on Hanford grouts are discussed.

A considerable data base exists on cemented waste forms leached in the intermittent solution exchange test. It is recommended that the ANS 16.1 test (ANS 1984) specifications be followed for performing the separate leach tests with the exception that representative groundwater be used as the leachant. ANS recommends that the ratio of the volume of the leachant to the surface area of the right cylinder waste forms be 10 cm. One-liter containers, which are convenient to use, thus require a grout surface area of 50-80 cm^2. The aspect ratio (length/radius of the waste form) should be 0.2 to 5.

For both the sediment column adsorption tests and the combined waste form experiment described in Section 7.0, special test considerations presented in Relyea 1982 and Relyea, Serne and Rai 1980 should be observed. These considerations include: 1) the column diameter should be at least 30 to 40 times the mean particle diameter of the sediment to avoid local velocity effects such as wall channeling; 2) the column length should be at least four times the column diameter to avoid sensitivity of the effective column porosity to flow rates; and 3) the Darcy velocity (flow rate) used in the experiment should be greater than $1.6 \times 10^{-3}/L$ cm/sec (L is the column length) to minimize migration of waste in the pore water due to diffusion.

The latter criterion imposes a rather high flow rate for column lengths normally employed (10 to 50 cm) when compared to the expected recharge rates in the Hanford vadose zone (0.5 to 5 cm/year, or 0.2 to 2×10^{-7} cm/sec).

Thus, the flow rate criterion appears to be incompatible should one want to run the experiment at near the expected flow rate for the Hanford site to allow slow chemical reactions to reach completion. Lengthy experiments using the expected flow rate would make diffusion an important component of the effluent migration rates. This would complicate data analysis. Until a better understanding of the interactions among grout, sediment and groundwater is developed, it is recommended that experiments be performed at flow rates intermediate between the expected field value and a faster value required to minimize the effects of diffusion.

The preliminary grout experiments are being performed under saturated conditions. The effects of partial saturation on the chemical reactions that may occur is presently unclear. The few data presented in Gee and Campbell 1980 and Routson and Serne 1972 suggest that Hanford sediments show the same adsorption distribution coefficients (Rd) for radionuclides studied under both saturated and partially saturated hydrologic conditions. On the other hand, Dayal, Schweitzer and Davis 1984 found that the release of Sr from low-level waste solidified in cement was significantly reduced in samples that were alternately wetted and dried in contrast to samples that remained immersed in water. Thus, additional work on adsorption under partially saturated conditions is recommended.

D. REDOX AND CO_2 GAS EQUILIBRIA

For the disposal of Hanford grouts in the vadose zone, the oxidation-reduction potential will probably remain oxidizing while chemical interactions occur between the grout, groundwater and sediment. Therefore, it is unlikely that special precautions will need to be taken to minimize the presence of air in the experiments. This simplifies the experimental design in that controlled-atmosphere chambers to house the experiments will not be necessary. On the other hand, the presence of air may be necessary to avoid depleting CO_2 in the leachant.

With the passage of time, unreacted hydrated lime [$Ca(OH)_2$] from the grout will react with CO_2 in the atmosphere or with CO_2, HCO_3^- and CO_3^{2-} dissolved in the groundwater. Past work (Opitz, Dodson and Serne 1985) on the

neutralization of uranium mill tailings with hydrated lime shows that different results are obtained depending on whether the systems are open or closed to contact with air. Work performed recently (and partially described in this letter report) on the leaching of grout also shows that the leachates obtained from open and closed leach vessels have distinctly different chemistry. (Radionuclide data from these ongoing tests are not yet available due to a backlog of samples that need counting, so the effects on these constituents cannot yet be determined.) An evaluation of whether CO_2 gas will be supplied to the disposed grout monolith at a rate that maintains CO_2 equilibrium conditions in the air-filled voids at the grout-sediment interface is needed. Ongoing experiments under saturated conditions may need to be modified to supply CO_2 at an adequate rate should CO_2 equilibrium prove to be a controlling factor.

E. EXTRAPOLATION OF DATA TO LONG TIME PERIODS

A significant issue in developing data for long-term performance assessment predictions is whether the relatively short duration laboratory experiments yield relevant data. The aging of grouts may either improve or degrade grout properties, resulting in significanty different rates of release of waste from those measured on freshly made grout.

A key in predicting the performance of grout waste forms over extremely long time periods (up to 10,000 years) requires an understanding of the grout properties at specific ages. Grouts must be produced that have the appropriate "aged" composition in a reasonable time for testing. However, methods for producing "old" samples have not been developed to a defensible state. Historically, the prediction of properties of radioactive waste materials has been attempted through the study of natural analogs. The basis for this comparison is that the analogs have been stable for thousands to millions of years; therefore their counterparts should also be stable. However, cementitious materials, such as grout, in comparison to the relatively static systems of nature, are actually dynamic systems since their chemical and physical properties change continually with time. While attempts have been made to study ancient cementitious materials (Roy and Langton 1983), direct comparison

with today's materials is impossible because of unknown starting compositions of the ancient mortars and different aging conditions.

A review of the literature pertaining to "accelerated testing" and "accelerated curing" revealed no directly applicable procedures that could be employed for predicting long-term performance of cemented waste forms. Most of the procedures cited in the references were intended solely for quality assurance of concretes in the construction industry. These methods are typically used to predict the 28-day compressive strength of concrete cylinders from samples that have been cured under accelerated conditions for times typically less than one day. The absolute strength after accelerated curing is not the same as the 28-day strength, but through comparison with actual 28-day strengths, a relationship is obtained that allows the prediction. These methods are not applicable to accelerated aging schemes since the very long time periods of concern in radioactive waste disposal precludes establishing a relationship between artificially aged samples and samples aged for thousands of years under ambient conditions.

One study does, however, appear to be applicable to the development of an accelerated aging scheme. The study of glass-reinforced cement materials by scientists at Pilkington Brothers Limited of England (Litherland, Oakley, and Proctor 1981; Oakley, Litherland and Proctor 1981; Proctor, Oakley and Litherland 1982; and Aindow, Oakley, and Proctor 1984) warrants a brief discussion. In an effort to determine the suitability and the long-term durability of these materials for the construction industry, a series of long-term laboratory tests were started in the late 1960's. A set of specimens was stored in the laboratory at temperatures ranging from room temperature to 100°C at 100% relative humidity. At the same time, many additional specimens were exposed to the weather of the United Kingdom. During the mid-to-late 1970's, specimens were also exposed to a variety of environments ranging from the dry desert of Arizona to the wet-dry cycles of Bombay. As the data were collected, a clear trend emerged between the strength of the material and the temperature. In this study, 50°C and 100% relative humidity were selected as the accelerating conditions. Acceleration factors of up to 1600 were found. That is, within a few days under these conditions, the same development in

strength properties was observed that was found in samples left in the natural environment for about ten years.

Under idealized conditions of constant temperature and humidity, portland cement undergoes most of its basic changes within a few years. These changes include hydration of the initial cement phases and conversion of metastable phases to phases more thermodynamically stable. Environmental factors may also cause changes in the normal cement phases. These may be caused by interactions between the grout and the groundwater and other factors unique to the disposal system such as radiation and decay heat. The effect of these environmental factors on the performance of the disposal system must be determined to predict overall system effectiveness over the time frame of concern. Since the basic and environmentally induced reactions are extremely slow after the first few months or years, methods of producing artificially aged samples must be developed and defended to provide data on the long-term performance of disposed grout.

The factors most likely to dominate the accelerated aging process in cementitious materials include temperature, pressure, and surface area. However, since there are many reactions that occur during the curing and subsequent hardening of cementitious materials, the rates of each reaction must be evaluated in order to effectively produce a material representative of a naturally aged sample.

Temperature has the strongest effect on the rates of hydration of the cement phases. However, the rates of reaction are not increased at the same level for all the phases and the actual hydrated species may have different stoichiometries at various elevated temperatures (Neville 1981). Pressure in itself is expected to have a minimal effect on the aging process. The time/temperature history of the cement also has a large influence on the phase composition and morphology. Cements that have been allowed to cure at room temperature prior to high temperature treatment contain largely different properties than those that are subjected to high temperatures immediately after mixing. Increased surface area (fineness) of cement acts as an accelerant by decreasing the diffusion path for water to hydrate the cement, thereby allowing for more rapid hydration of the unreacted particles.

Essentially complete hydration of the major cement phases can occur within seven days by continually ball milling a cement/water slurry (Neville 1981). This technique may be useful in determining the chemical nature of the hydrated species; however, the physical changes and interactions can only be implied.

Scouting tests are necessary to identify and optimize valid accelerating conditions. Since the purpose of the testing scheme is to predict properties of very old materials, methods must be identified which effectively compress the time scale of aging without changing the natural reaction mechanisms. Through the Hanford Grout Technology Program, PNL is performing scouting tests; the data from which is intended to establish the necessary conditions for conducting further, more system-specific grout aging tests during later testing phases.

The scouting tests involve the conditioning of small grout cylinders in constant humidity chambers at elevated temperatures. At specified times (i.e., 7, 14, 28 days, 2, 3, 6 and 12 months) a few samples being conditioned at various temperatures are characterized for mineralogy, density, porosity and strength. The data will be analyzed to determine the times and elevated temperatures that cause the same kinds of mineralogic and physical changes as caused by long-term aging under ambient temperature conditions at 100% relative humidity.

Other scouting studies will involve conditioning thin wafers of grout and larger grout samples in contact with soils saturated with water at two elevated temperatures. The wafer samples are expected to age more quickly as groundwater can more rapidly penetrate and completely react with this sample. At selected times, these sample will be characterized as described previously.

Currently it is premature to recommend protocols for producing artifically aged grout or conducting accelerated leach tests and combined leach-adsorption tests. The scouting studies and analyses underway are intended to identify those factors that control the long-term performance of grout disposed in Hanford soil. The ultimate goal of this work is the development of a protocol(s) that can be used to generate data useful for predicting long-term grout performance.

7.0 DESCRIPTION OF FIRST COMBINED EXPERIMENT

Results from an ongoing laboratory experiment are discussed in this section. Interpretations of the available data from this experiment reported herein are preliminary and subject to change as more data become available. The experiment, in which a 0.5 liter grout cylinder was packed in a coarse Hanford sediment and subsequently leached with Hanford groundwater, is described. This combined experiment is related to numerous separate experiments on grout leaching and sediment adsorption being performed at PNL under the auspices of the Hanford Grout Technology Program. In these experiments, the same grout, sediment, and groundwater are used. The separate experiments involve only two components each, either grout and groundwater (a leach test) or leachate and sediment (an adsorption test). Because these separate tests are being used to compare performance with the combined test, some of the separate test results will also be presented. The results of these separate tests have not yet been formally documented, but should appear in a topical report in FY-1986. An important objective of the combined test is to evaluate whether the characteristics of the resulting effluent solutions can be adequately explained by the results of the two-component leaching and adsorption tests.

A. COMBINED TEST CONFIGURATION

The combined test involves a cylinder of grout surrounded by a coarse Hanford sediment which is packed in a vertical column. Hanford groundwater is passed through the column, across the surface of the grout, through a layer of sediment, and into a collection vessel. The individual components of the test are described in this section.

A.1 Radioactive Grout

The grout waste form used in this experiment was made from a low-level liquid waste stream identified as Hanford Facilities Waste (HFW). HFW is comprised predominantly of phosphate and sulfate solutions that result, respectively, from a decontamination operation and a fuels storage basin water

cleanup process at N Reactor. The phosphate solution used to produce the grout waste form was actual N Reactor waste and contained measurable activities of ^{54}Mn and ^{60}Co. The sulfate solution used was a chemically simulated liquid waste spiked with ^{85}Sr and ^{137}Cs. The composition of the HFW grout is shown in Table 1. A ratio of seven pounds of grout-forming solids per gallon of liquid (840 g/L) was used to produce the grout.

TABLE 1. Composition of Radioactive Hanford Facilities Waste Grout

	Material	Fraction
Solids	Portland Type I and II Cement	41 wt%
	Class F Fly Ash	40 wt%
	Attapulgite Clay	11 wt%
	Indian Red Pottery Clay	8 wt%
Liquids	Sulfate Waste Components	40 vol%
	0.03 M Na_2SO_4	
	0.01 M NaOH	
	0.02 M $NaNO_2$	
	Phosphate Waste Components	60 vol%
	0.151 M Na_3PO_4	
	0.013 M $NaNO_2$	
	0.01 M NaOH	

After curing at room temperature in capped plastic containers for about six months, the 0.5 L right cylinder grout blocks were removed from their containers and their physical dimensions and weight were measured. The blocks were then installed in the column test apparatus that was subsequently sealed to prevent drying of the grout.

A.2 Hanford Sediment

The sediment used for this study was obtained from the new AP Tank Farm excavation in the 200 East Area and represents expected sediments in the nearby grout disposal site. The sediment is being characterized for particle size and hydrologic characteristics. It is also being used in lysimeter field demonstrations involving Hanford grouts. The sediment sample was air dried and well mixed prior to its use in the laboratory experiments.

A.3 Hanford Groundwater

Using data from the Hanford Groundwater Monitoring Program, a well was identified on the Hanford site that is uncontaminated and provides water representative of natural waters in the unconfined aquifer underlying Hanford. Periodically large volumes of water are pumped from the well (#6 S3 25) into pre-rinsed plastic containers which are brought back to the laboratory. The well water is filtered through a 0.45 μm membrane and stored for use in the laboratory experiments. A complete chemical analysis of the water is made on each new batch. No significant changes in the water composition from batch to batch and during storage in the laboratory have been observed. The chemical composition is shown in Tables 2 and 3 with other data from the column tests.

A.4 Column Description

Two column experiments are under way. Each column contains one 0.5 liter grout block (right cylinder, d = 10.8 cm and L = 5.5 cm). In one experiment, the grout block is suspended in the middle of a 13.8 cm diameter x 15.0 cm long plexiglass column. The grout is suspended in a nylon mesh bag in the upper 1/3 of the column. Inlet and outlet tubes in the column end caps are used to add leachant (Hanford groundwater) and to collect leachate, respectively. The leachant flows into the bottom of the column, around the grout block and out the top at a volumetric flow rate of 0.20 ml/hr. The linear velocity through the column is 1.7×10^{-3} cm/hr or about 15 cm/year. This rate is 3 to 30 times faster than the range of recharge rates used in the Hanford Defense Waste Environmental Impact Statement (HDW-EIS).

TABLE 2. 0.5 Liter Grout and Sediment/Hanford Groundwater

	Units	Well Water	#1	#2	#3	#4	#5	#6	#7	#8	#9[a]	#10
pH	--	8.1	8.62	7.86	8.31	8.78	8.79	8.77	8.67	8.74	8.84	8.84
Eh	mv	295	394	376	382	364	301	334	330	371	299	328
Al	mg/ℓ	<0.1	<0.03	<0.03	<0.03	0.09	<0.03	<0.03	<0.03	<0.03	6.01	<0.03
Ba	mg/ℓ	0.06	0.05	0.03	0.03	0.047	0.029	0.020	0.021	0.016	0.018	0.012
Ca	mg/ℓ	56	34.8	41.7	43.7	38.4	30.8	26.5	26.4	21.8	15.1	24.10
Cd	mg/ℓ	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cr	mg/ℓ	<0.015	<0.015	<0.015	<0.015	0.371	<0.015	<0.015	<0.015	<0.015	0.053	<0.015
Cu	mg/ℓ	<0.005	<0.005	<0.005	<0.005	<0.015	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Fe	mg/ℓ	<0.01	0.026	0.025	<0.005	0.006	<0.005	0.026	0.020	0.014	<0.005	<0.005
K	mg/ℓ	7.8	9.57	6.76	6.30	6.60	6.64	6.20	6.13	5.82	37.92	5.42
Mg	mg/ℓ	14.4	19.43	10.13	8.88	8.95	8.76	8.09	7.79	7.07	3.15	6.52
Mn	mg/ℓ	<0.01	<0.3	<0.3	0.3	0.25	<0.3	0.005	0.008	0.14	<0.005	0.009
Na	mg/ℓ	25	70.8	63.0	65.8	67.7	73.1	73.64	75.12	73.8	268.8	73.82
P	mg/ℓ	<0.1	0.58	0.18	0.26	0.49	0.48	0.81	0.81	0.78	0.57	0.81
(as PO_4)	mg/ℓ	<0.3	1.78	0.55	0.80	1.50	1.47	2.48	2.48	2.39	1.75	2.48
Pb	mg/ℓ	<0.05	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
S	mg/ℓ	28.34	32.36	30.58	27.40	21.57	21.92	19.22	18.46	17.14	21.35	14.90
(as SO_4)	mg/ℓ	85	97.1	91.7	82.2	64.7	65.8	57.59	55.31	51.40	63.96	44.64
Si	mg/ℓ	15	26.8	25.6	25.0	24.14	25.44	24.54	25.42	26.53	20.08	26.51
Sr	mg/ℓ	0.25	0.40	0.23	0.21	0.202	0.192	0.179	0.172	0.154	0.130	0.145
Zn	mg/ℓ	<0.01	<0.005	<0.005	<0.005	0.096	0.126	<0.005	<0.005	0.264	<0.005	<0.005
F^-	mg/ℓ	<0.5	<10	<10	<10	<2	<2			<2		<2
Cl^-	mg/ℓ	22	38	38	32	10.7	11.2			10.8		10.8
NO_2^-	mg/ℓ	<0.03	<0.4	<0.8	<0.4	<0.5	<0.5			<0.5		<0.5
NO_3^-	mg/ℓ	0.1	4	4	4	<1	<1			<1		<1
SO_4^{2-}[b]	mg/ℓ	86	139	124	103	48	48			34		26
HCO_3	mg/ℓ	171	246.6	209.3	232.4	223.7	211.1	230.0	233.1	208.1	225.5	226.0
CO_3^{2-}	mg/ℓ	2.1	5.1	0.8	2.3	6.6	0.1	6.7	5.4	5.6	7.6	2.9
OH^-	mg/ℓ	0	0	0	0	0	0	0	0	0	0	0
B	mg/ℓ	0.06	0.23	0.20	0.21	0.35	0.32	0.36	0.35	0.40	0.68	0.40
(as H_3BO_3)	mg/ℓ	0.35	1.32	1.14	1.20	2.00	1.83	2.06	2.00	2.29	3.89	2.28
PO_4[b]	mg/ℓ	<1.0	<10	<10	<10	<10	<10			<10		<10
TOC	mg/ℓ	1.0	21.8	13.7	15.5	16.2	15.8	18.7	19.3	15.0	20.7	20.2
Cations	meq/ℓ	5.28	6.67	5.84	5.94	5.77	5.61	5.21	5.40	5.03	13.7	5.10
Anions	meq/ℓ	5.28	7.43	6.50	6.55	5.74	5.53			4.80		4.85
Total mls			42	71	109	146	182	219	254	286.5	321.5	359.5
Mls to mid point			21	56.5	90	127.5	164	200.5	236.5	270.2	304	340.5
Time (hrs)			238.5	432	625.2	811	979	1174	1345.5	1531	1680.5	1896.2
Pore Volume (Sediment upstream only)			0.04	0.10	0.16	0.22	0.28	0.35	0.41	0.47	0.53	0.59

(a) This sample is suspect and is likely mislabeled.
(b) Data from IC analysis is a check on ICP data reported above. ICP are more accurate and used in all calculations.

TABLE 3. 0.5 Liter Grout/Hanford Groundwater

	Units	Well Water	#1	#2	#3	#4	#5	#6	#7	#8	#9[a]	#10
pH	--	8.1	9.79	11.47	11.43	12.10	11.28	11.57	11.82	12.01	11.07	12.80
Eh	mv	295	384	347	343	307	277	257	294	313	308	290
Al	mg/ℓ	<0.1	4.47	8.05	9.23	9.79	10.63	10.64	10.80	11.25	6.05	11.95
Ba	mg/ℓ	0.06	0.002	0.008	0.010	0.030	0.017	0.014	0.015	0.030	0.015	0.026
Ca	mg/ℓ	56	1.12	0.76	0.84	1.22	0.82	0.52	0.61	1.83	15.06	1.18
Cd	mg/ℓ	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cr	mg/ℓ	<0.015	0.053	0.070	0.077	0.096	0.100	0.081	0.077	0.119	0.050	0.091
Cu	mg/ℓ	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Fe	mg/ℓ	<0.01	<0.005	<0.005	<0.005	<0.005	0.021	0.004	<0.005	0.043	0.06	<0.005
K	mg/P	7.8	39.1	51.3	57.2	58.6	63.66	65.96	66.75	65.11	38.3	69.84
Mg	mg/ℓ	14.4	0.18	<0.10	<0.10	<0.1	0.12	<0.1	<0.1	<0.1	3.14	<0.1
Mn	mg/ℓ	<0.01	<0.3	<0.3	<0.3	0.013	<0.3	<0.01	<0.01	0.017	0.01	0.054
Na	mg/ℓ	25	255.4	344.4	385.6	390.1	429.4	430.9	436.4	440.1	271.19	485.4
P	mg/ℓ	<0.1	<0.10	0.161	0.223	0.263	0.221	0.340	0.330	0.372	0.390	0.258
(as PO_4)	mg/ℓ		<0.3	0.49	0.68	0.81	0.68	1.04	1.01	1.14	1.19	0.79
Pb	mg/ℓ	<0.05	<0.05	<0.05	<0.05	0.03	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
S	mg/ℓ	28.34	29.15	28.53	27.45	26.28	27.46	25.05	24.93	26.09	21.50	28.54
(as SO_4)	mg/ℓ	85	87.3	85.5	82.2	78.7	82.3	75.0	75.0	78.2	64.4	85.5
Si	mg/ℓ	15	12.2	12.0	12.1	13.86	13.38	12.59	13.24	14.72	20.22	16.59
Sr	mg/ℓ	0.25	0.08	0.09	0.10	0.18	0.10	0.10	0.11	0.12	0.13	0.19
Zn	mg/ℓ	<0.01	<0.005	<0.005	<0.005	0.007	0.075	<0.005	<0.005	4.03	<0.005	0.005
F^-	mg/ℓ	<0.5	<10	13	13	14	14			13		13
Cl^-	mg/ℓ	22	32	29	29	12.7	13.1			17.5		12.5
NO_2^-	mg/ℓ	<0.03	8.5	23	26	15.6	17.0			17.0		17.0
NO_3^-	mg/ℓ	0.1	<4	<4	<4	<1	<1			2.2		<1
SO_4^{2-}[b]	mg/ℓ	86	110	103	88	59	61			54		56
HCO_3	mg/ℓ	171	394.2	0	0	0	0	0	0	0	0	0
CO_3^{2-}	mg/ℓ	2.1	187.9	265.7	382.3	181.4	200.4	428.4	352.8	312.0	528.0	300.0
OH^-	mg/ℓ	0	0	44.1	40.4	161.6	214.5	71.4	121.4	142.8	40.8	166.6
B	mg/ℓ	0.06	0.53	0.70	0.78	0.87	0.90	0.93	0.91	1.03	0.68	0.40
(as H_3BO_3)	mg/ℓ	0.35	3.03	4.00	4.46	4.98	5.15	5.32	5.20	5.87	3.89	2.28
PO_4[b]	mg/ℓ	<1.0	<10	<10	<10	<10	<10			<10		
TOC	mg/ℓ	1.0	15.7	104.4	106.7	102.7	112.9	108.0	106.0	108.3	106.1	105.5
Cations	meq/ℓ	5.28	12.18	16.33	18.27	18.52	20.35	20.45	20.90	20.89	13.8	21.0
Anions	meq/ℓ	5.28	14.88	15.23	18.90	18.20	21.90			21.50		22.4
Total mls			33	70	105	154	189	223	260	295	334	372
Mls to mid point			16.5	51.5	87.5	129.5	171.5	206	241.5	277.5	314.5	353
Time (hrs)			193.8	405.5	573	811	979	1153.5	1316	1508	1704.5	1896

(a) This sample is suspect and is likely mislabeled.
(b) Data from IC analysis is a check on ICP data reported above. ICP are more accurate and used in all calculations.

In the second column experiment, a grout block of the same composition and dimensions is situated in the lower part of the column. The grout block is supported on a 1.3 cm thick layer of Hanford sediment. Additional sediment is packed around the grout block and fills the remaining void space at the top of the column. Hanford groundwater is pumped into the bottom of the column where it flows through the bottom layer of sediment, around the grout, and through the upper layer of sediment. The volumetric flow rate is 0.11 ml/h which is equivalent to a linear velocity of 1.6×10^{-3} cm/hr or about 14 cm/year in an empty column. This value is 2.8 to 28 times faster than the range of recharge rates used in the HDW-EIS. Assuming a particle density for the sediment of 2.7 g/cm^3 and given that the weight of soil used was 3042.08 g, the bulk density of sediment is 1.72 g/mc^3 and the sediment porosity is 0.36. Thus, the actual pore velocity in the sediment is $1.6 \times 10^{-3}/0.36 = 4.44 \times 10^{-3}$ cm/hr.

B. EFFLUENT COLLECTION

In both experiments, the effluent is collected in a sealed container to minimize evaporation and loss or gain of CO_2. In the beginning of the experiments, aliquots were collected after approximately every 30 milliliters of effluent generation. Each aliquot is further split into 4 samples which are analyzed for (a) Eh, pH, alkalinity, (b) major cations and selected trace metals, (c) major anions, inorganic carbon and organic carbon, and (d) radionuclide content. The aliquots are not filtered because the column effluent ports are covered by very fine nylon mesh that is effective for removing most suspended particulates. Thus, we are assuming that the solution analyses represent only dissolved and colloidal species.

C. RESULTS AND DISCUSSION

Chemical compositions of the effluents from the two column experiments are shown in Tables 2 and 3. These experiments are continuing and, as shown in Table 2, only about 0.6 pore volume of effluent has been collected. As additional effluent is collected, compositions may change. The data collected to date show that the effluent from the column experiment involving both grout

and sediment is buffered at a pH of between 8.0 and 8.8 whereas the effluent from the grout-only experiment quickly rose to the 11-12 range. Both effluents show a reduction in calcium and magnesium concentrations relative to their levels in the Hanford groundwater leachant. The reduction of calcium and magnesium levels in the grout-only experiment is nearly quantitative. It is speculated that calcium and magnesium are precipitating on and in the solid grout as a carbonate phase. However, the carbonate/bicarbonate concentrations do not show a comparable drop which appears inconsistent with this assessment. Separate ANS 16.1 intermittent solution exchange and static leach tests on smaller grout blocks, however, do show a comparable drop in carbonate and bicarbonate concentrations. This discrepancy needs an evaluation. Sodium and potassium concentrations in the grout-only effluent are increased greatly over the Hanford groundwater concentrations, whereas only the sodium is increased in the combined experiment. The release of sodium and potassium is expected as they are very soluble elements contained in the grout. Sodium is the major component of the liquid HFW and is likely in solution in the free liquid trapped in the pores of the grout. Potassium is likely being released by the fly ash and cement and is also probably present in the HFW.

HFW contains high concentrations of phosphate, sulfate and nitrite anions. Because anions are typically very mobile in sediments, they are expected to migrate if released from the grout. Table 3 shows that the leachate from the half-liter grout block in the grout-only experiment contains a small amount of phosphate but shows little change in sulfate relative to the starting level in the groundwater. Phosphate levels have increased in both effluents, but moreso in the combined test effluent. The nitrite concentration rapidly and substantially increased in the grout-only leachate but has not been measurable in the combined experiment effluent. It is especially intriguing that no nitrite has been observed in the combined test effluent. Sulfates and phosphates can enter into various precipitation reactions with alkaline-earths in sediments, but nitrite should be relatively unreactive. As nitrate is a very mobile constituent in Hanford sediments as evidenced by the nitrate plumes below the 200 Areas, more study will be necessary to explain the difference in nitrite data from these two experiments.

The grout-only effluent contains about five times the level of dissolved organic carbon as contained in the combined test effluents. The primary component of the dissolved organic carbon is likely citrate which is known to be present in the phosphate waste. As with nitrite, the sediment appears to inhibit migration of organic carbon.

The total dissolved solids contents of the two effluents are also significantly different. Aside from the initial effluent (Samples 1 through 5 of Table 2) and Sample 9, the effluent from the combined test shows a net loss of dissolved salts versus the leachant (Hanford groundwater). This observation is based on a comparison of the total milliequivalents of cations and anions in solution. The slight increase in total dissolved solids initially is likely due to flushing of evaporites from the Hanford sediment. When dried, most Hanford sediments retain evaporites that are readily released upon rewetting. The sudden spurt of dissolved solids in Sample 9 (Table 2) has not yet been explained, but may be due to sample mislabeling or analytical deficiencies. (Note that Sample 9 data from each test (Tables 2 and 3) look alike and there appears to be little relationship to Sample 8 and 10 data.) The combined test appears to show net precipitation in the test column, whereas the grout-only test is showing net dissolution. The last several aliquots of grout-only effluent (with the exception of Sample 9) contain about four times the level of dissolved solids as the Hanford groundwater. The last several aliquots of the dissolved test effluent contain a slightly lower level of dissolved solids relative to the groundwater solids.

If ion exchange adsorption were the sole reaction occurring between leachate and sediments in the combined test, one would not expect to see a measurable decrease in total dissolved solids. The ion exchange adsorption of a leached species onto sediment would result in the release of a comparable amount (based on charge) of material from the sediment. Thus, it appears that there are distinct differences in the chemical reactions occurring among the various tests.

The radionuclide content of the two effluents is shown in Table 4. To date, no measurable quantities of radionuclides have been detected in the effluents from the combined test. The activity of ^{137}Cs and ^{85}Sr in the

TABLE 4. Radionuclide Content of Effluents (nCi/L) from Grout Column Experiments

Sample No.	^{54}Mn	^{60}Co	^{85}Sr	^{137}Cs
	Grout-Only Column			
1	<d.l.	<d.l.	3.55	60.0
2	N/A	N/A	N/A	N/A
3	<d.l.	<d.l	3.12	89.5
4	N/A	N/A	N/A	N/A
5	<d.l	<d.l	4.63	106.0
6	N/A	N/A	N/A	N/A
7	<d.l.	<d.l.	4.96	106.0
8	<d.l.	<d.l.	4.73	104.0
9	<d.l	<d.l.	5.79	109.0
	Grout Plus Sediment Column			
1	<d.l.	<d.l.	<d.l.	<d.l.
2	N/A	N/A	N/A	N/A
3	<d.l.	<d.l.	<d.l.	<d.l.
4	N/A	N/A	N/A	N/A
5	<d.l.	<d.l.	<d.l.	<d.l.
6	N/A	N/A	N/A	N/A
7	<d.l.	<d.l.	<d.l.	<d.l.
8	<d.l.	<d.l.	<d.l.	<d.l.
9	<d.l.	<d.l.	<d.l.	<d.l.

<d.l. = below detection limit
N/A = sample has not yet been analyzed

effluents in the grout-only test appear to rise rapidly to steady-state values. No measurable ^{60}Co or ^{54}Mn activities are present. It is not surprising that no radioactivity has been found in the effluent from the combined test because only 0.6 pore volumes of solution have passed through the column. It is anticipated that many pore volumes must be passed through the column before breakthough of the radionuclides occurs.

Preliminary adsorption tests (both batch and once-through column) have been performed from ANS 16.1 intermittent solution exchange leach tests under the Hanford Grout Technology Program using HFW grout leachate. The chemical composition of leachate from the ANS 16.1 leach tests (pH 8.5 to 9.0) is similar to the effluent compositions shown in Table 2. The preliminary batch adsorption tests yielded Rd values of 91 ± 2 ml/g and 1400 ± 120 ml/g for Sr and Cs, respectively. The batch Rd values for Mn and Co were not quantifiable because of the very low levels originally present in the ANS 16.1 leachate. However, a qualitative assessment of the data suggests that significant adsorption of Mn and Co occurred.

In a related tests, a large batch of the ANS 16.1 leachate was fortified with additional ^{85}Sr and ^{137}Cs and pumped through a small column filled with Hanford sediment. The column dimensions are 3.2 cm dia. x 12.5 cm length. The Hanford sediment was packed into the column to a bulk density of 1.6 g/cm^3. Assuming the particle density is 2.7 g/cm^3, the column pore volume is about 40 ml. A flow rate of ~ 2 ml/h was maintained for the first 65 pore volumes and then the flow rate was increased to ~ 7 ml/h. At 127 pore volumes the flow rate was again reduced to 2 ml/h where it continues. At selected pore volumes, the ph, Eh, total chemical analysis and radionuclide content were measured. Table 5 shows the total chemical analysis and Figure 1 shows the measured breakthrough curve for ^{85}Sr, the only one of the four radionuclides that has been found in the effluent.

The chemical composition of the early effluent samples shows an initial release of calcium, magnesium, strontium, chloride, sulfate and bicarbonate. These chemicals represent evaporites that are flushed from the sediment. In sample PV 6 through the last sample measured (PV 144), minor fluxuations among the major cation concentrations are likely due to cation exchange

TABLE 5. Rd Adsorption Column

	Units	Tracer Influent	1 PV	2 PV	6 PV	10 PV	14 PV	18 PV	22 PV	26 PV	36 PV	46 PV	61 PV	73 PV	82 PV	93 PV	107 PV	120 PV	144 PV
pH	--	7.70	7.74	8.40	8.35	8.56	8.38	8.33	8.16	8.27	7.82	7.61	8.54	8.43	8.15	8.32	8.45	7.60	8.27
Eh	mv	308	396	387	392	330	357	316	411	269	401	392	374	375	386	382	342	382	266
Al	mg/ℓ	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.04	<0.03	<0.03	<0.03
Ba	mg/ℓ	0.037	0.14	0.06	0.04	0.03	0.03	0.04	0.04	0.04	0.04	0.01	0.033	0.040	0.038	0.038	0.034	0.031	0.038
Ca	mg/ℓ	27.8	176.0	83.8	49.1	46.8	46.7	47.2	43.9	44.0	42.0	39.7	39.2	37.1	37.0	34.7	31.8	30.3	32.0
Cd	mg/ℓ	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cr	mg/ℓ	<0.015	<0.015	<0.03	<0.05	0.03	0.04	0.04	<0.015	<0.015	<0.015	<0.015	0.050	<0.015	<0.015	<0.015	0.003	<0.0015	<0.0015
Cu	mg/ℓ	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.01	<0.01	<0.01	<0.01	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Fe	mg/ℓ	<0.002	<0.01	<0.01	0.03	<0.01	<0.01	0.03	<0.01	<0.01	0.017	<0.005	0.007	0.016	0.031	<0.01	<0.01	<0.01	<0.01
K	mg/ℓ	9.5	9.9	6.2	5.3	5.4	5.1	5.5	6.5	7.0	7.7	8.8	9.2	8.9	8.6	9.1	9.2	8.8	9.5
Mg	mg/ℓ	14.0	40.6	16.7	9.3	9.1	9.1	9.1	8.5	8.6	8.9	10.3	11.2	11.4	12.0	11.8	11.6	12.1	14.5
Mn	mg/ℓ	<0.05	<0.05	0.26	0.37	0.29	0.25	<0.05	0.1	0.1	0.1	<0.1	0.05	0.18	0.09	0.12	0.05	0.06	<0.05
Na	mg/ℓ	50.9	50.0	28.40	47.2	54.6	55.5	51.1	53.8	55.5	50.3	54.3	51.4	51.2	51.2	52.4	53.1	52.6	51.8
P	mg/ℓ	5.61	0.1	<0.1	2.0	3.90	4.28	4.58	5.4	5.5	5.0	4.4	5.36	5.83	5.40	6.03	6.36	5.58	4.53
P (as PO_4)	mg/ℓ	17.20	0.3	<0.3	6.1	12.2	13.1	14.0	16.6	16.9	15.3	13.5	16.4	17.9	16.6	18.5	19.5	17.1	13.9
Pb	mg/ℓ	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.05	<0.05	<0.05	<0.05	<0.05	0.05	0.12	<0.05	<0.05	<0.05
S (as SO_4)	mg/ℓ	88.6	151.8	104.2	92.7	95.1	89.5	88.9	92.0	93.1	89.2	94.4	91.4	92.3	90.4	95.6	99.4	95.4	88.7
Si	mg/ℓ	14.95	26.9	23.7	22.2	21.5	20.3	18.7	19.4	19.6	18.1	17.9	16.8	16.3	16.3	15.6	15.2	14.6	16.0
Sr	mg/ℓ	0.19	0.95	0.40	0.23	0.22	0.21	0.22	0.21	0.21	0.21	0.17	0.19	0.18	0.18	0.17	0.16	0.16	0.18
Zn	mg/ℓ	0.011	<0.01	<0.01	0.01	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.092	0.016	0.011	0.012	<0.01	<0.01	0.01
F^-	mg/ℓ	<2.0	11	<1.4	<1.4	<1.4	<1.4	<1.4	<0.4	<0.4	<1	<1	<2	<2	<2	<2	<2	<2	
Cl^-	mg/ℓ	14.9	23	20	20	20	20	20	22	22	23	31	14.4	14.2	22	14.4	14.7	14.7	
NO_2^-	mg/ℓ	<0.5	<0.6	1.2	<0.2	<0.2	<0.2	4.8	<0.3	3.2	3.7	9.8	<0.6	<0.5	<0.3	<0.5	<0.5	<0.5	
NO_3^-	mg/ℓ	21	<0.25	5.5	<0.25	7.6	10.1	10.1	15	9.1	10	4	12	20	26	15	18	17	
SO_4^{2-}	mg/ℓ	72	85	86	85	85	85	84	83	83	82	106	69	69	89	67	70	70	
HCO_3^-	mg/ℓ	128	390	188.4	166.1	152.6	148.5	154.9	--	149.5	161.9	173.2	150.5	137.2	168.4	352.5	118.6	145.8	157.0
CO_3^{2-}	mg/ℓ	0	1.6	2.3	1.8	2.7	1.8	1.6	--	1.4	3.3	3.0	2.6	1.8	1.2	3.6	1.6	0.3	0.8
PO_4^{3-}	mg/ℓ	13	<0.5	<0.5	4.6	7.3	8.8	8.2	27	27	14	17	13	13	12	13	13	12	
B	mg/ℓ	0.09	0.10	--	0.15	0.09	--	--	0.10	0.10	0.09	0.08	0.17	0.15	0.13	0.50	0.51	0.48	0.10
TOC	mg/ℓ																		
Cations	meq/ℓ	5.0	14.6	7.0	5.4	5.6	5.6	5.5	--	6.5	5.2	5.4	5.3	5.2	5.6	5.2	5.1	5.0	
Anions	meq/ℓ	5.2	10.8	6.8	5.4	5.5	5.4	5.6	--	5.9	5.9	6.5	6.3	6.2	6.2	7.4	3.7	4.0	

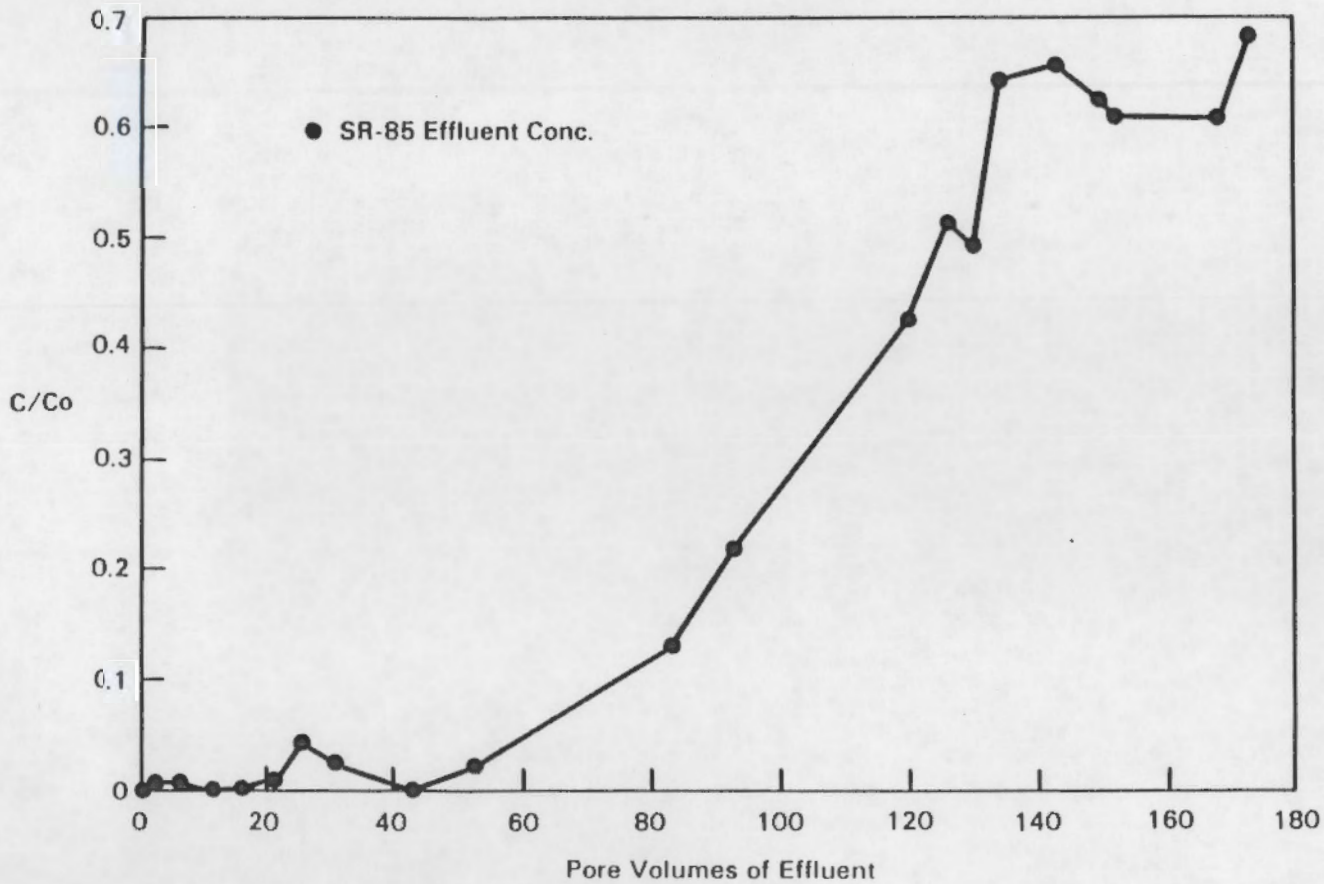

FIGURE 1. Breakthrough Curve for ^{85}Sr from Column Rd Adsorption Test

redistribution and dissolution of calcite. (The designation, PV, refers to pore volume.) In general, there appear to be no significant unexplained reactions. The anion data show that the phosphate present in the leachate starts evolving from the column during the 10th to 26th pore volume. Phosphates can interact with sediments even though they are anionic. Thus, the delay in their release was not unexpected. The nitrate data are peculiar in that the nitrate concentrations are very sporadic until the 73rd pore volume when levels stabilize at approximately the influent concentration. The measurable concentrations of nitrite in the 18th through 46th pore volume is strange because nitrite is below the detection limit in the influent solution. Nitrate reduction to nitrite is not expected in this environment. Also nitrate interaction with the sediment is not expected.

From Rd theory discussed in Section 5 (Relyea 1982 and Relyea, Serne and Rai 1980), one finds that for a constant input of a tracer to a column, a 0.5 breakthrough (C/C_0 = 0.5, where C = effluent concentration and C_0 = influent concentration) should occur at the pore volume equal to 1 + (bd/θ) Rd, where bd = sediment column bulk density (g/cm^3) and θ = sediment column porosity. The Rd column had a bulk density of 1.6 g/cm^3 and a calculated porosity of 0.407. As mentioned, the batch Rd experiment with this Hanford sediment and ANS 16.1 leachate gave a Rd (Sr) value of 91 cm^3/g. Therefore, the pore volume for 50% breakthrough should be [1 + (1.6/0.407) 91] = 358 pore volumes. Figure 1 shows the actual observed breakthrough curve. The column data start to show Sr breakthrough at between 30 and 60 pore volumes, reaching 0.5 breakthrough at about 130 pore volumes. There is no breakthrough of ^{137}Cs which agrees with the batch Rd data (Rd for Cs = 1400 ml/g). The lack of any ^{60}Co and ^{54}Mn in the column effluent also indicates high sorption coefficients for these elements. The fact that the column shows earlier breakthrough (at PV = 130 vs. 358) for Sr than the batch experiment is often observed (see Serne and Relyea 1983). The exact cause for differences in batch and column adsorption experiments has not been resolved, but likely includes effects of varying the solution-to-solid ratio used in the two tests. The solution-to-solid ratio in the batch experiment was 30 ml:1g whereas the column ratio was 0.407 ml:1g. At any rate, none of the four radionuclides present in the HFW grout being studied show signs of rapid migration in Hanford sediments.

8.0 RECOMMENDATIONS

In this section, plans for additional analyses of data from the ongoing experiments are described. Recommendations are also given for additional types of studies that could improve our understanding of the chemical reactions occurring among the grout, sediments, and groundwater and our ability to predict performance of the grout disposal system.

A. ADDITIONAL ANALYSES

As part of the Hanford Grout Technology Program, numerous two-component leach tests have been underway since January 1985. Two of these tests, the ANS 16.1 and static tests, are showing two distinctly different chemical systems, as are the grout-only and combined grout and sediment column tests. A key to the differences seems to be the supply of HCO_3^- or dissolved CO_2 supplied to the systems. There is a difference of at least 3.5 pH units between the two leach systems. The pH of the ANS 16.1 leachates is ~ 8.5 and the pH of the static leachates is 12.0. At the higher pH values, calcium and magnesium are essentially removed from the solution, likely as carbonate minerals.

At the end of the leaching experiments, the solid grout samples will be dried and sectioned to allow exploration of the mineralogic and radionclide content as a function of distance from the surface. Further, the leach solution analyses will be analyzed by a geochemical code (i.e., MINTEQ - Felmy et al. 1984) to identify which minerals might be at equilibrium with the solution. If the MINTEQ-predicted mineral concentrations agree with the concentrations actually measured, then the controlling dissolution-precipitation reactions are likely identified. The geochemical code can also project what minerals might form over long time periods and aid in projecting how grout ages. Where solubility control is indicated, an excess of the solubility-controlled chemical will be added to the leach tests to evaluate whether the resulting equilibrium returns to the predicted level.

Adsorption tests have not been performed using the more basic (pH = 12) leachates. Some batch Rd tests should be performed to evaluate whether there are any significant differences.

The existing Rd adsorption column will be dissected and the distribution of ^{60}Co, ^{54}Mn, ^{137}Cs and ^{85}Sr determined. A measure of the distance from the front of the column to where 50% of the mass was adsorbed can be used to estimate an Rd. Gross mineralogic changes in the sediments will also be determined.

The solution flow rates in the two 0.5 liter grout column experiments will likely be increased. These experiments will be stopped after several months and mineralogic and radionuclide content analyses will be performed on the grout and sediment.

The leaching data will be analyzed by the semi-infinite solid effective diffusion theory discussed in Section 4. The resulting data from the combined grout-sediment test will be compared to simple "waste package" models described by Chambré and Pigford (1984) and Zavoshy, Chambré and Pigford (1985).

B. ADDITIONAL EXPERIMENTS

If the supply rate of CO_2 is shown to be a key to data interpretations, experiments in which CO_2 content is increased should be attempted. Experimentation in a partially saturated environment with elevated partial pressures of CO_2 may accelerate prediction of the effects of CO_2. Until the mechanisms of leaching and the subsequent interactions with sediments are better elucidated, it is difficult to suggest specifics on combined grout/groundwater/sediment tests. The apparent significant differences between the two grout column tests suggest that combined tests may give the most accurate demonstration of the performance of grout disposal system. On the other hand, at this early stage, interpretation of the results and identification of the controlling processes remains a challenge. Without more understanding of the controlling processes, it will be difficult to defend a particular methodology or to select the most realistic conditions for testing. A wide range of conditions for testing exists involving issues such as as waste form size versus amount of sediment, leachant flow rate and residence time, partial saturation or saturation, and open or closed to the atmosphere. It is hoped that the analyses yet to be performed on the separate leaching and adsorption tests and

the combined test will provide knowledge on controlling processes and shed light on what parameters should be considered as most important in designing experiments to provide the data upon which long term performance assessments are based.

Current tests are based on six-month old samples of grout. Aged grouts are likely to exhibit different properties when tested under simulated disposal conditions. A credible methodology should include grouts that have been artifically aged if predictions of long-term performance are to be made.

REFERENCES

Aindow, A. J., D. R. Oakley, B. A. Proctor. 1984. "Comparison of the Weathering Behavior of GRC with Predictions Made from Accelerated Aging Tests," Cement and Concrete Research. 14:271-274.

ANS. 1984. Measurement of the Leachibility of Solidified Low-Level Radioactive Wastes, ANS 16.1, American Nuclear Society, Champaign, Illinois.

Arora, H. and R. Dayal. 1984. Solidification and Leaching of Boric Acid and Resin LWR Wastes. NUREG/CR-3909, Nuclear Regulatory Commission, Washington, D.C.

Brandstetter, A., et al. 1979. Waste Isolation Safety Assessment Program Technical Progress Report for FY-1978. PNL-2874, Pacific Northwest Laboratory, Richland, Washington.

Brown, D. J. 1959. Subsurface Geology of the Hanford Separations Areas. HW-61780, General Electric Company, Richland, Washington

Burkholder, H. C., et al. 1979. Waste Isolation Safety Assessment Program - Technical Progress Report for FY-77. PNL-2642, Pacific Northwest Laboratory, Richland, Washington.

Chambré, P. L. and T. H. Pigford. 1984. "Prediction of Waste Performance in a Geologic Repository," in Scientific Basis for Nuclear Waste Management VIII, editor G. L. McVay, Elsevier Science Publishing Company, Inc., New York, New York, pp. 985-1008.

Claassen, H. D. 1981. "Conceptual Models Governing Leaching Behavior and Their Long-Term Predictive Capability," Nuclear and Chemical Waste Management. 2:307-313.

Clark, W. E. 1977. "The Isolation of Radioiodine with Portland Cement Part 1: Scoping Leach Studies," Nucl. Tech. 36:215-221.

Coles, D. G. 1981. "A Continuous-Flow Leach Testing Method for Various Nuclear Waste Forms," Nuclear and Chemical Waste Management 2:245-252.

Coles, D. G., H. C. Weed, D. D. Jackson and J. S. Schweiger. 1978. "Single-Pass Leaching of Nuclear Melt Glass by Groundwater," in Radioactive Waste in Geologic Storage, editor S. Fried, ACS Symposium Series 100, American Chemical Society, Washington, D.C., pp. 93-103.

Coles, D. G. and L. D. Ramspott. 1982. "^{106}Ru Migration in a Deep Tuffaceous Alluvium Aquifer, Nevada Test Site: Discrepancy Between Field Observations and Prediction from Laboratory Measurements. Science 215:1235-1237.

Columbo, P. 1983. Leaching Properties of Solidified TRU Contaminated Incinerator Ash. BNL-33671, Brookhaven National Laboratory, Upton, New York.

Daniels, W. R., et al. 1981. Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media, October 1, 1979-September 30, 1980. LA-8586-PR, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

Dayal, R., H. Arora and N. Morcos. 1983. Estimation of Cesium-137 Release from Waste/Cement Composites Using Data From Small-Scale Specimens, NUREG/CR-3382, Nuclear Regulatory Commission, Washington, D.C.

Dayal, R., D. C. Schweitzer and R. E. Davis. 1984. "Wet and Dry Cycle Leaching: Aspects of Research in the Unsaturated Zone," in NRC Nuclear Waste Geochemistry '83 edited by D. H. Alexander and G. F. Birchard, NUREG/CP-0052, Nuclear Regulatory Commission, Washington, DC, pp. 440-453.

Deutsch, W. J., E. A. Jenne and K. M. Krupka. 1982. "Solubility Equilibria in Basalt Aquifers: The Columbia Plateau, Eastern Washington, U.S.A.," Chemical Geology, 36:15-34.

Felmy, A. R., D. C. Girvin and E. A. Jenne. 1984. MINTEQ: A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA-600/3-84-032 available from NTIS PB84-157148. Environmental Protection Agency, Athens, Georgia.

Francis, C. W., M. Reeves III, E. A. Bondietti, and B. A. Smith. 1979. "Chromatographic Kd Values of Radionuclides and the Effect of Redox Potentials on Sorption of Radionuclides by Geologic Media." Task 4 Third Contractor Information Meeting, J. F. Relyea, ed., Vol. 1, pp. 435-525. PNL-SA-7352, Pacific Northwest Laboratory, Richland, Washington.

Francis, C. W., M. Reeves III, R. S. Fisher, and B. A. Smith. 1978. "Soil Chromatograph Kd Values." Waste Isolation Safety Assessment Program, Task 4 Contractor Information Meeting Proceedings, R. J. Serne, ed., pp. 403-421. PNL-SA-6957, Pacific Northwest Laboratory, Richland, Washington.

Gee, G. W. and A. C. Campbell. 1980. Monitoring and Physical Characterization of Unsaturated Zone Transport: Laboratory Analysis. PNL-3304, Pacific Northwest Laboratory, Richland, Washington.

Gee, G. W., A. C. Campbell, P. J. Wierenga, and T. L. Jones. 1981. Unsaturated Moisture and Radionuclide Transport: Laboratory Analysis and Modeling. PNL-3616, Pacific Northwest Laboratory, Richland, Washington.

Godbee, H. W., O. U. Anders, and R. M. Neilson, Jr. 1980. "Application of Mass Transport Theory to the Leaching of Radionuclides from Waste Solids," Nuclear and Chemical Waste Management. 1:29-35.

Hagglund, K. M. and P. G. Hagan (editors). 1982. Standardization of Methods for Measuring Migration of Radionuclides in Geomedia, TL084-4, Transuranics Waste Systems Office, Rockwell International, Rocky Flats, Colorado.

Harada, M., et al. 1980. Migration of Radionuclides Through Sorbing Media, Analytical Solutions-I. LBL-10500, Lawrence Berkeley Laboratory, Berkeley, California.

Heller, P. R., G. W. Gee and D. A. Meyers. 1985. Moisture and Textural Variations in Unsaturated Soils/Sediments Near the Hanford Wye Barricade. PNL-5377, Pacific Northwest Laboratory, Richland, Washington.

Inoue, Y. and W. J. Kaufman. 1963. "Prediction of Movement of Radionuclides in Solution Through Porous Media." Health Phys. 9:705-715.

Kaiser Engineers Hanford Company. 1985. "Conceptual Design Report - Grout Disposal Facilities - Project B-566," KEH-84-58, Richland, Washington.

Kalb, P. D. and P. Columbo. 1984. "Full-Scale Leaching Study of Commercial Reactor Waste Forms," in Waste Management '84, Vol. 2, edited by R. G. Post, The University of Arizona Press, Tempe, Arizona, pp. 189-194.

Lea, F. M. 1971. The Chemistry of Cement and Concrete. Chemical Publishing Co., New York.

Litherland, K. L., D. R. Oakley and B. A. Proctor. 1981. "The Use of Accelerated Aging Procedures to Predict the Long Term Strength of GRC Composities." Cement and Concrete Research. 11:455-466.

Machiels, A. J. and C. Pescatore. 1981. "The Influence of Surface Processes in Waste Form Leaching," in Scientific Basis for Nuclear Waste Management, Vol. 3. Editor J. G. Moore, Plenum Press, New York, New York, pp. 371-378.

Matsuzuru, H. and A. Ito. 1977. "Immobilization of Cesium-137 in Cement-Waste Composites by Addition of Mineral Zeolites," Health Physics 34:643-648.

Matsuzuru, H. and N. Moriyama. 1982. "Leaching Radionuclides from a Cement Composite Incorporating Evaporator Concentrates Generated at a Pressurized Water Reactor Nuclear Power Plant," Nuclear Science and Engineering 80:14-25.

MCC. 1985a. Nuclear Waste Materials Handbook: Test Methods. DOE/TIC-11400, Pacific Northwest Laboratory, Richland, Washington.

MCC. 1985b. Test Methods Submitted for Nuclear Waste Materials Handbook, PNL-3990, Pacific Northwest Laboratory, Richland, Washington.

McHenry, J. R. 1957. Properties of Soils of the Hanford Project. HW-53218, General Electric Company, Richland, Washington.

Mendel, J. E. 1982. "The Measurement of Leach Rates: A Review," Nuclear and Chemical Waste Management 3:117-123.

Meyer, R. E. 1979. "Systematic Study of Metal Ion Sorption on Selected Geologic Media." Task 4 Second Contractor Information Meeting, R. J. Serne, ed., Vol. 1, pp. 231-239. PNL-SA-7352, Pacific Northwest Laboratory, Richland, Washington.

Meyer, R. E., et al. 1981. "Systematic Study of Nuclide Adsorption on Selected Geologic Media." Waste/Rock Interactions Technology Program, FY-80 Information Meeting, J. F. Relyea, ed., pp. 151-182. PNL-3887, Pacific Northwest Laboratory, Richland, Washington.

Meyer, R. E., S. Y. Shiao, P. Rafferty, J. S. Johnson, jr., I. L. Thomas, and K. A. Kraus. 1978. "Systematic Study of Nuclide Sorption on Selected Geologic Media." Waste Isolation Safety Assessment Program, Task 4 Contractor Information Meeting Proceedings. R. J. Serne, ed., pp. 343-369. PNL-SA-6957, Pacific Northwest Laboratory, Richland, Washington.

Moody, J. B. 1981. Radionuclide Migration/Retardation: Research and Development Technology Status Report. ONWI-321, Office of Nuclear Waste Isolation, Columbus, Ohio.

Moore, J. G., H. W. Godbee and A. H. Kibbey. 1977. "Leach Behavior of Hydrofracture Grout Incorporating Radioactive Wastes." Nuclear Technology, 32:39-59.

Moriyama, N., S. Dojiri and H. Matsuzuru. 1977. "Leaching of ^{137}Cs from the Ion Exchange Resin Incorporated in Polyethylene or Cement Composite," Health Physics 32:549-552.

Moriyama, N., H. Matsuzuru, S. Dojiri, and Y. Wadachi. 1975. Analytical Evaluation on the Leaching of Radionuclides from Waste Solids. JAERI-M 6302. Japan Atomic Energy Research Institute, Tokyo, Japan.

Muller, A. B., D. Langmuir, and L. E. Duda. 1983. "The Formulation of an Integrated Physiocochemical-Hydrologic Model for Predicting Waste Nuclide Retardation in Geologic Media." In Scientific Basis for Waste Management VI, D. G. Brookins, ed., Materials Research Society Symposium Proceedings, Vol. 15, pp. 547-564.

Muller, A. B., D. Langmuir and I. Neretnieks. 1984. "Conclusions from an NEA Workshop: The Role of Phenomenological Sorption Modeling in Performance Assessment of Radioactive Waste Disposal Systems," in Scientific Basis for Nuclear Waste Management VII, G. L. McVay, ed., Elsevier Science Publishing Company, Inc., New York, New York, pp. 817-826.

NEA. 1983. Sorption Modeling and Measurement for Nuclear Waste Disposal Studies, RWM-4, Nuclear Energy Agency, Paris, France.

Nestor, C. W., Jr. 1980. Diffusion from Solid Cylinders. ORNL/CSD/TM-84. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Neville, A. M. 1981. Properties of Concrete. Third Edition. Pitman Publishing Inc., Marshfield, Massachusettes.

Nielson, D. R. and J. W. Biggar. 1961. "Miscible Displacement in Soils: I. Experimental Information." Soil Sci. Amer. Proc. 25:1-5.

Oakley, D. R., K. L. Litherland, and B. A. Proctor. 1981. "The Development of a Method of Predicting the Weathering Behavior of Glass Reinforced Cement Composites," in the Proceedings of the Second International Conference on Durability of Building Materials and Components, Gaithersburg, Maryland, pp. 225-231.

Opitz, B. E., M. E. Dodson and R. J. Serne. 1985. Uranium Mill Tailings Neutralization: Contaminant Complexation and Tailings Leaching Studies, NUREG/CR-3906, U.S. Nuclear Regulatory Commission, Washington, D.C.

Passioura, J. B. and D. A. Rose. 1971. "Hydrodynamic Dispersion in Aggregated Media II. Effects of Velocity and Aggregate Size." Soil Sci. 111:354-352.

Peterson, S. R., R. J. Serne, A. R. Felmy, R. L. Eriskon, K. M. Krupka and G. W. Gee. 1984. "Interactions of Acidic Solutions with Sediments: A Case Study," in Proceedings of NRC Nuclear Waste Geochemistry '83, editors D. H. Alexander and G. F. Birchard, NUREG/CP-0052, Nuclear Regulatory Commission, Washington, DC, pp. 513-535.

Pigford, T. H., et al. 1981. Migration of Radionuclides Through Sorbing Media Analytical Solutions-II. LBL-11616, Lawrence Berkeley Laboratory, Berkeley, California.

Proctor, B. A., D. R. Oakley, and K. L. Litherland. 1982. "Developments in the Assessment and Performance of GRC over 10 Years," Composites, Butterworth and Co. Ltd.

Reardon, R. J. 1981. "Kd's - Can They be Used to Describe Reversible Ion Sorption Reaction in Contaminant Migration?" Ground Water 19:279-286.

Relyea, J. F. 1982. "Theoretical and Experimental Considerations for the Use of the Column Method for Determining Retardation Factors," Rad. Waste Man. and the Nucl. Fuel Cycle. 3:115-130.

Relyea, J. F., R. J. Serne and D. Rai. 1980. Methods for Determining Radionuclide Retardation Factors: Status Report. PNL-3349, Pacific Northwest Laboratory, Richland, Washington.

Richardson, G. L. 1981. "The Phantom Dissolution Leach Model," Nuclear and Chemical Waste Manual. 2:237-241.

Routson, R. C. and K. R. Fecht. 1979. Soil (Sediment) Properties of Twelve Hanford Wells with Geologic Interpretation. RHO-CD-82, Rockwell Hanford Operations, Richland, Washington.

Routson, R. C. and R. J. Serne. 1972. One-Dimensional Model of the Movement of Trace Radioactive Solute Through Soil Columns: The PERCOL Model. USAEC report, BNWL-1718, Battelle, Pacific Northwest Laboratory, Richland, Washington.

Roy, D. M. and C. A. Langton. 1982. Longevity of Borehole and Shaft Sealing Materials: 2. Characterization of Cement-Based Ancient Building Materials. ONWI-202, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio.

Roy, D. M. and C. A. Langton. 1983. Characterization of Cement-Based Ancient Building Materials in Support of Repository Seal Materials Studies. BMI/ONWI-523, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio.

Sambell, R.A.J., C. Smitton and A. Elsden. 1982. "A Contribution Towards a Standard Leach Test for Immobilized Low and Medium Level Waste," Nuclear and Chemical Waste Management, 3:125-129.

Serne, R. J. and J. F. Relyea. 1983. "The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program." In The Technology of High-Level Nuclear Waste Disposal, Vol. 1, DOE/TIC-4621, pp. 203-254, Technical Information Center, U.S. Department of Energy, Washington, D.C.

Serne, R. J., R. C. Routson, and D. A. Cochran. 1974. Experimental Methods for Obtaining PERCOL Model Input and Verification Data. USAEC Report, BNWL-1721, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D. M., K. M. Krupka and B. E. Grambow. 1984. "Solubility Interpretations of Leach Tests on Nuclear Waste Glass," Nuclear and Chemical Waste Management 5:87-99.

Travis, C. C. 1978. Mathematical Description of Adsorption and Transport of Reactive Solutes in Soil: A Review of Selected Literature. ORNL-5403, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Treat, R. L., R. O. Lokken, S. L. Stein, and C. A. Geffen. 1985. "Operational and Long-Term Performance Assessment for Hanford Grout." Proceedings of the Symposium on Waste Management, Tucson, Arizona, March 24-28, 1985, pp. 497-501.

Triolo, R., N. Harrison and K. A. Kraus. 1979. "Use of the Axial Filter to Measure Low Distribution Coefficients," J. Chromatography. 197:19-35.

Tsang, C. F. and D. C. Mangold (ed). 1984. Panel Report on Coupled Thermo-Mechanical-Hydro-Chemical Processes Associated with a Nuclear Waste Repository, LBL-18250, Lawrence Berkeley Laboratory, Berkeley, California 94720.

Van Genuchten, M. Th., J. M. Davidson, and P. J. Wierenga. 1974. "An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement in Porous Media." Soil Sci. Soc. Am. Proc. 38:29-35.

Van Genuchten, M. Th., P. J. Wierenga, and G. A. O'Conner. 1977. "Mass Transfer Studies in Sorbing Porous Media: III. Experimental Evaluation with 2,3,5-T." Soil Sci. Soc. Am. J. 41:278-285.

Weed, H. C. and D. D. Jackson. 1979. Design of a Variable Flow-Rate, Single Pass Leaching System. UCRL-52785, Lawrence Livermore National Laboratory, Livermore, California 94550.

Westsik, J. H., C. O. Harvey, F. P. Roberts, W. A. Ross and R. E. Thornhill. 1983. "Comparison of 200 Liter and 400 Milliliter Leach Tests," in Scientific Basis for Nuclear Waste Management VI, Editor D. G. Brookins, Elsiever Publishing Inc., New York, New York, pp. 243-249.

Zavoshy, S. J., P. L. Chambré and T. H. Pigford. 1985. "Mass Transfer in a Geologic Environment," in Scientific Basis for Nuclear Waste Management VIII, editors C. M. Jantzen, J. A. Stone, R. C. Ewing, Materials Research Society, Pittsburgh, Pennslyvania, pp. 311-322.