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THE SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT
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PERMEABILITY, SWELLING AND RADIONUCLIDE RETARDATION PROPERTIES OF CANDIDATE BACKFILL MATERIALS*

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ABSTRACT

A backfill placed between a nuclear waste canister and the host geology of a nuclear waste repository can impede the migration of water through the waste package and retard the movement of radionuclides into the geologic formation. Hydraulic conductivities and swelling pressures are being determined as functions of the density of the compacted backfill, temperature, radiation dose, hydraulic head and the chemical composition of the permeating fluid. Bentonite clays and bentonite/sand mixtures have received initial emphasis. Sodium bentonite and calcium bentonite samples compacted to a dry density of 2.1 g/cm^3 had hydraulic conductivities in the range of 10^{-12} to 10^{-13} cm/s. In addition, batch distribution ratios (R_d) for Sr, Cs, Am, Np, I, U and Tc have been measured for a number of candidate backfill materials. Both initial permeability and sorption studies have used a synthetic basaltic ground water.

INTRODUCTION

Concepts currently under investigation for the disposal of high-level nuclear wastes include deep emplacement of the wastes in continental geologic formations. Such a disposal method would incorporate a waste package placed within the geologic medium. A backfill barrier, emplaced between the containerized waste and the host rock, can both protect the other engineered barriers and act as a primary barrier to the release of radionuclides from the waste package. A properly designed backfill should 1) retard or exclude the migration of ground water between the host rock and the waste canister system; 2) retard the migration of selected chemical species (corrosive agents and radionuclides) in the ground water; and 3) control the Eh and pH of the ground water within the waste-package environment [1,2,3].

Candidate backfill materials that have the above attributes have been selected and are being evaluated as part of the Development of Backfill Materials Program sponsored by the Office of Nuclear Waste Isolation under its contract with the U.S. Department of Energy [1]. Tests are being conducted to determine the following for potential backfill materials: permeabilities, sorption capacities, compaction properties, thermal conductivities, and long-term stabilities in thermal and radiation environments. This paper presents the initial results of our investigations into the ability of candidate backfill

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materials to impede the migration of water, and to slow or eliminate radionuclide movement in the event that water is able to enter the structural barriers and leach the wastes.

RETARDATION OF WATER MIGRATION

The ability of the backfill to slow or stop water movement is related to the permeability and swelling potential of the material. Obviously, the lower the permeability the smaller the quantity of water that could potentially reach the structural barriers and eventually the wastes. Furthermore, the swelling of a clay component within the backfill may plug cracks in the waste package and surrounding host rock. Experiments are being conducted to determine the permeability and swelling pressures of several backfill materials.

Permeabilities, or more appropriately, hydraulic conductivities, are being calculated by using Darcy's law for flow through porous media [4]. In this empirical relation, the volumetric flow rate is proportional to the hydraulic gradient across the medium:

$$Q = -KAh \qquad (1)$$

where
- Q = the volumetric flow rate;
- A = the cross-section area of the sample;
- h = the hydraulic gradient across the sample;
- K = a constant called the hydraulic conductivity.

This hydraulic conductivity is dependent on the properties of both the porous medium and the permeating fluid. It can be related to the specific permeability, k, which is dependent only on the properties of the porous medium, by the equation

$$K = \frac{k\rho g}{\mu} \qquad (2)$$

where
- ρ and μ = the density and viscosity of the permeating fluid;
- g = the acceleration due to gravity.

Hydraulic conductivities for various candidate backfills are determined using the apparatus shown in Figure 1. The permeating fluid is pumped by a high-pressure pump into the permeability cell. The fluid is dispersed on the face of the backfill by a porous metal disk. After flowing through the backfill and out of the permeability cell, the fluid is collected in a preweighed vessel. The volumetric flow rate is determined by weighing the effluent as a function of time. The hydraulic head is measured with a pressure transducer just ahead of the permeability cell. The outlet pressure is assumed to be atmospheric. In the initial tests, the powdered backfill sample was placed in the permeability cell and pressed to the desired density. All the initial permeability tests were conducted with samples compacted to a measured density of 2.1 g/cm^3. The density was measured before the test was started. It is, therefore, an unsaturated density with the samples containing 5 to 7% water. Eventually, hydraulic conductivities will be determined at several compaction densities.

Sodium and calcium bentonites and sodium bentonite/quartz sand mixtures have been tested. A synthetic basaltic ground water with a composition similar to ground waters found in the Grande Ronde formation beneath the Hanford site has been used as the permeating fluid [5]. Table I shows the results of these tests. Sodium bentonite, with a hydraulic conductivity of less than 10^{-12} cm/s,

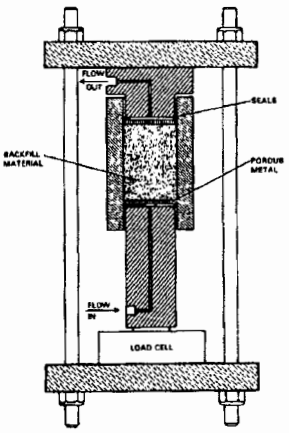

Fig. 1. Schematic of permeability cell

was the least permeable of the materials tested. As quartz sand was added, the permeability of the mixture increased. A 50 wt% clay/50 wt% sand mixture had a hydraulic conductivity of 5 x 10^{-12} cm/s, and a 25% clay/75% sand mixture had a hydraulic conductivity of 7 x 10^{-10} cm/s. Calcium bentonite was more permeable than sodium bentonite; its hydraulic conductivity was about 1.5 x 10^{-12} cm/s. Over the range of hydraulic heads applied, the hydraulic conductivity was constant for each material.

Our measured hydraulic conductivities should overestimate the ground water flow for the small gradients expected within a repository. Because of the low permeabilities of the materials being tested, large hydraulic heads must be applied to obtain meaningful results within reasonable lengths of time. It has been reported that permeabilities of swelling clays, such as bentonite, increase as the hydraulic gradient is increased and that some deviations from Darcy's law are observed at very low hydraulic gradients [6,7,8]. The net effect is that flow rates in a repository would be slower than predicted by extrapolating our experimental results to smaller hydraulic heads.

The design life of the backfill can be conveniently divided into two periods. The first period, prior to saturation of the backfill, is one of complete water exclusion. During the second period, after saturation of the backfill, movement of water through the backfill will be controlled by the hydraulic properties of the backfill materials and by the regional hydraulic gradient.

The length of the first period--the time required for water to reach the containerized waste--will depend upon how rapidly water can migrate through the host rock to the backfill and the time required for water to soak through the unsaturated backfill material. The time required for water to migrate to the

TABLE I
Permeability tests summary

Backfill Material	Density (g/cm^3)	Head (MPa)	Hydraulic Gradient	Time (h)	Hydraulic Conductivity (cm/s)	Swelling Pressure (MPa)
Na Bentonite	2.05	15.5	1.56×10^5	269	---	
		6.9	6.95×10^4	46	---	
		20.7	2.09×10^5	316	6.7×10^{-13}	
	2.13	14.6	1.56×10^5	766	5.6×10^{-13}	58
		20.4	2.14×10^5	504	5.5×10^{-13}	57
		7.1	7.46×10^5	846	4.6×10^{-13}	58
Ca Bentonite	2.09	20.7	2.13×10^5	858	1.3×10^{-12}	
	2.11	15.4	1.59×10^5	617	1.6×10^{-12}	31
		20.7	2.16×10^5	506	1.5×10^{-12}	31
		7.0	7.22×10^4	837	1.3×10^{-12}	
50% Na Bentonite 50% Sand (80-120 mesh)	2.12	15.5	1.62×10^5	192	4.6×10^{-12}	
		6.9	7.18×10^4	46	3.3×10^{-12}	
		20.7	2.15×10^5	1011	4.0×10^{-12}	
	2.09	16.7	1.73×10^5	618	6.4×10^{-12}	21
		20.7	2.13×10^5	504	5.4×10^{-12}	21
		7.1	7.31×10^4	484	4.5×10^{-12}	
25% Na Bentonite 75% Sand (80-120 mesh)	2.10	3.4	1.19×10^4	1222	6.6×10^{-10}	
50% Volclay saline seal 50% Sand (80-120 mesh)	2.22	15.2	1.66×10^5	169	4.1×10^{-12}	
		6.9	7.55×10^4	72	---	
		3.4	3.78×10^4	67	3.5×10^{-12}	
		6.9	7.55×10^4	72	3.1×10^{-12}	
		20.7	2.27×10^5	97	3.1×10^{-12}	
		15.5	1.70×10^5	334	2.9×10^{-12}	

backfill will depend upon the site geology and upon thermal and hydraulic gradients around the waste package. The time required to saturate the backfill is a complex function of clay properties, particularly for highly compacted montmorillonites (bentonites), and will require careful experimental evaluation.

The second period relates to the time required for a significant volume of water to reach the canister system, equilibrate with the system, and then continue to migrate down the hydraulic gradient. If a canister-overpack is assumed to be 1 m OD x 3 m high, then the volume of such a cylinder is 2.36 m^3, and the external surface area is 11 m^2. It is assumed that ground water approaches the cylinder through 50% of the surface area and recedes from the cylinder through the remaining 50% of the surface area. If a conservative regional hydraulic gradient of 1.0 cm H_2O/cm length, and a conservative hydraulic conductivity of 1×10^{-11} cm/s are applied to this example, the additional time required for the first "equivalent volume" of ground water to contact the cylinder after ground water finally reaches the cylinder in this simple model is 1×10^5 years. This

equivalent volume, equal to the volume of the cylinder, is relatively small and probably would not result in significant waste package degradation.

Swelling pressures are measured simultaneously with the hydraulic conductivities. The load cell in the permeability apparatus shown in Figure 1 is used to follow the pressure buildup as the clay saturates. The actual swelling pressures reported in Table I were determined by turning off the pumps and reducing the hydraulic head to zero before reading the swelling pressure. The magnitude of the hydraulic head to which the clay was exposed prior to the measurement apparently had no effect on the observed swelling pressure. The swelling pressure remained constant during 3 months of testing. Sodium bentonite exhibited the largest swelling pressure. With a measured water-saturated density of approximately 2.3 g/cm^3, the swelling pressure agreed favorably with that reported earlier by Pusch [9].

RETARDATION OF RADIONUCLIDE MIGRATION

The second most important attribute for a backfill material is its ability to retard the migration rate of selected chemical species [1]. In this role, the backfill slows or eliminates radionuclide release from the waste package when or if the structural barrier system fails and water is able to leach radionuclides from the waste material. The retardation ability of the backfill may also slow the inward movement of chemical species that produce corrosion of the structural barriers; however, the importance of this remains to be evaluated and will depend upon both the host geology and the materials selected for the canister and overpack.

Radionuclide retardation can occur by several processes such as ion exchange, chemisorption, precipitation and redox reactions [10]. For our materials-screening needs, the laboratory batch retardation methodology provided a rapid and cost-effective method of comparing a wide variety of potential backfill materials for their selective retardation of specific radionuclides. Batch sorption experiments involve contacting a sample of water that contains the radionuclide under investigation with a small weighed sample of solid material. After steady state is reached, a "distribution ratio," R_d, is determined:

$$R_d = \frac{C_s}{C_\ell}, \ cm^3/g \qquad (3)$$

where

C_s = the concentration of radionuclide sorbed in or on the solid phase (g/g of solid);
C_ℓ = the concentration of radionuclide remaining in the liquid phase (g/cm^3 of solution).

The distribution ratio (R_d) generated by these batch sorption experiments is a measure of the overall ability of the solid phase to remove the radionuclide from solution. The data are reported as distribution ratios (R_d) rather than distribution coefficients (K_d's) because more than one mechanism may be involved and the reversibility of the mechanisms has not been demonstrated.

Batch sorption experiments are usually related to the behavior of dynamic systems by the relationship [11]

$$K = 1 + \frac{\rho K_d}{\varepsilon} \qquad (4)$$

where

K = ratio of bulk ground water velocity to nuclide velocity (dimensionless);
ρ = solid bulk density (g/cm^3);
ε = void fraction or porosity (dimensionless);
K_d = distribution coefficient (cm^3/g).

This relationship is based upon the assumption of reversibility of sorption and, thus, may not be completely applicable in these tests. For this reason, a series of dynamic (column) experiments, designed to directly measure the retardation of nuclides, will be carried out in conjunction with the permeability measurement described earlier.

Batch distribution ratios (R_d) have been determined for several commercially available materials being evaluated as backfill components. Radionuclides used are those that have been identified as posing the greatest potential hazard to man during long-term storage of nuclear waste [10,11]. Samples of each material were contacted with a synthetic basalt ground water doped with tracer quantities of a single radionuclide [5]. The initial pH of the ground water was 9.85, and the contact times were 14 and 28 days. No attempt has been made to determine the reversibility of the reactions measured. The results are shown in Table II.

TABLE II
Representative batch distribution (R_d) ratios for backfill candidates

Material	Distribution Ratio, R_d							Final pH
	^{85}Sr	^{137}Cs	^{241}Am	^{237}Np	^{125}I	^{233}U	^{99}Tc	
Coconut Charcoal	979	8	1.2E5	583	8.3E3	290	1.5E4	8.9
Iron (powder)	320	9	1.2E5	710	2.4	9.2E3	2.2E4	8.7
13-X, powder (faujacite)	6.0E4	1.8E3	[illegible]	18	1.2	194	0.8	9.4
4A, powder (Type A)	2.0E4	1.0E3	---	11	0.4	---	0.8	10.1
Calcium Bentonite	865	1.1E5	9.2E3	78	1.5E-3	76	0.9	8.2
Sodium Bentonite	6.8E3	1.0E3	1.4E3	29	1.4E-3	8	---	8.6
AW-400 (erionite)	2.3E4	6.7E4	92	13	0.8	7	1.2	8.5
AW-500 (chabazite)	2.3E3	7.8E4	1.3E3	18	1.5	17	0.9	8.4
Zeolon-900 (mordenite)	1.5E4	8.3E4	24	12	1.8	35	1.6	8.6

The results show that Sr, Cs and Am are strongly sorbed by clays and some zeolites; that Am, Np, I and Tc are strongly sorbed by charcoal; and that Am, Np, U, and Tc interact strongly with iron metal. The term sorbed is used herein to include all processes which adsorb or sequester the radionuclide into or onto the solid phase. Results to date suggest that nuclides such as Sr, Cs, and Am are adsorbed by materials with large cation-exchange capacities via ion-exchange processes. The strong interactions of Np, U, and Tc with iron powder suggests that the metallic iron is reducing these multivalence elements to highly insoluble forms and that precipitation may be the dominate mechanism for removing them from solution [12]. These results suggest that, if analysis of backfill performance indicates that higher retardation factors are required, then additives are available that will sorb radionuclides of interest.

SUMMARY

A properly designed backfill can function as more than a simple filler in the volume between containerized waste and the host material of a geologic repository. Materials can be selected that will slow the flow of water through the backfill and that will retard the migration of radionuclides from the waste. Experiments have been initiated to measure the permeabilities of candidate backfill materials and particularly bentonite clays. Other tests have determined the ability of several materials to sorb radionuclides of importance in the long-term performance of the waste package. The results to date indicate that a backfill can serve as an effective barrier to the release of radionuclides from a functioning waste package. Potential backfill materials will continue to be tested for permeabilities and sorption capabilities and will also be evaluated in terms of important parameters such as thermal conductivity and long-term stability in thermal and radiation fields.

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PNL-SANDIA HLW PACKAGE INTERACTIONS TEST: PHASE ONE

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ABSTRACT

The first phase of a complex high-level waste (HLW) package interactions test in a salt environment has been completed. The test system consisted of PNL 76-68 HLW glass (loaded with inactive fission products and ^{238}U) surrounded by a stainless steel waste canister, a TiCode-12 overpack, a bentonite/sand backfill, excess brine leachant, and a bedded rock salt container, all held within a 19-liter autoclave. All components were physically compromised in order to force wasteform-barrier-salt interactions to occur during this 95-day, 250°C overtest. Analyses of leachant, wasteform, and all barrier surfaces were performed. Test data included the synergistic effects between barriers and confirmed previous analyses of simpler systems. The glass wasteform exhibited some surface alteration but was not dissolved to any significant degree. The TiCode-12 overpack showed minimal uniform corrosion and no localized attack. Observed mineralogical alteration of the backfill was minimal.

INTRODUCTION

The National Waste Terminal Storage (NWTS) program has research efforts underway to select appropriate wasteforms and engineered barrier materials for nuclear waste packages for geologic disposal. These efforts include selection of package components to perform specific functions, testing of their interactions under expected repository environments, and overtests thereof.

Waste package development programs have narrowed the list of candidate materials for input to conceptual waste package design efforts. It is important to determine as early as possible in the development and design effort whether significant negative interactions can occur between candidate waste package components. This can be evaluated by allowing or forcing components to interact with each other through solution contact and under accelerated test conditions and noting any significant alteration and/or degradation of component properties.

This paper reports the results of the first HLW package interactions test that combined all components of a conceptual HLW package design under the appropriate test environment of a repository in salt.

The objectives of this complex test were to:

1. Acquire a large body of empirical data on HLW package interactions in an accelerated time frame under conditions of non-credibly severe failure of backfill, overpack, and canister barriers. (It must be emphasized that this test was an intentionally severe overtest, conducted for the purpose of maximizing interactions, not for the purpose of representing expected repository conditions.)