

LOAN DOCUMENT

DTIC ACCESSION NUMBER	PHOTOGRAPH THIS SHEET	INVENTORY																										
	LEVEL																											
	Permeable Barriers Materials for Strontium Immobilization: - UFA Determination . . . DOCUMENT IDENTIFICATION 1996																											
DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited																												
DISTRIBUTION STATEMENT																												
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td colspan="2" style="text-align: center;">ACCESSION FOR</td> </tr> <tr> <td style="width: 50%;">NTIS</td> <td style="width: 50%;">ORAAI</td> </tr> <tr> <td>DTIC</td> <td>TRAC</td> </tr> <tr> <td>UNANNOUNCED</td> <td></td> </tr> <tr> <td>JUSTIFICATION</td> <td></td> </tr> <tr> <td colspan="2" style="height: 20px;"></td> </tr> <tr> <td colspan="2" style="height: 20px;"></td> </tr> <tr> <td colspan="2" style="height: 20px;"></td> </tr> <tr> <td colspan="2">BY</td> </tr> <tr> <td colspan="2">DISTRIBUTION/</td> </tr> <tr> <td colspan="2">AVAILABILITY CODES</td> </tr> <tr> <td style="width: 50%;">DISTRIBUTION</td> <td style="width: 50%;">AVAILABILITY AND/OR SPECIAL</td> </tr> <tr> <td style="height: 40px; vertical-align: middle; text-align: center;">A-1</td> <td></td> </tr> </table>			ACCESSION FOR		NTIS	ORAAI	DTIC	TRAC	UNANNOUNCED		JUSTIFICATION								BY		DISTRIBUTION/		AVAILABILITY CODES		DISTRIBUTION	AVAILABILITY AND/OR SPECIAL	A-1	
ACCESSION FOR																												
NTIS	ORAAI																											
DTIC	TRAC																											
UNANNOUNCED																												
JUSTIFICATION																												
BY																												
DISTRIBUTION/																												
AVAILABILITY CODES																												
DISTRIBUTION	AVAILABILITY AND/OR SPECIAL																											
A-1																												
DATE RECEIVED IN DTIC																												
19980710 085																												
DATE RECEIVED IN DTIC																												
PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-FDAC																												

HANDLE WITH CARE

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 074-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE Sept 96	3. REPORT TYPE AND DATES COVERED Technical Report.	
4. TITLE AND SUBTITLE Permeable Barrier Materials for Strontium Immobilization: UFA Determination of Hydraulic Conductivity, Column Sorption Experiments			5. FUNDING NUMBERS N/A	
6. AUTHOR(S) T.E. Moody and J. Conca				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) CH2M HILL Hanford, Inc. Northwest Environmental Services Testing and Training			8. PERFORMING ORGANIZATION REPORT NUMBER BHI-00857 Rev.0	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203			10. SPONSORING / MONITORING AGENCY REPORT NUMBER N/A	
11. SUPPLEMENTARY NOTES Report prepared for the US DOE Office of Environmental Restoration and Waste Management. This work was supported in part by DOE. The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein. All other rights are reserved by the copyright owner.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution is unlimited			12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 Words) Selected materials were tested to emulate a permeable barrier and to examine the (1) capture efficiency of these materials relating to the immobilization of strontium-90 and hexavalent chromium in Hanford groundwater and (2) hydraulic conductivity of the barrier material relative to the surrounding area. The emplacement method investigated was a permeable reactive barrier to treat contaminated groundwater as it passes through a barrier. The hydraulic conductivity function was measured for each material, and retardation column experiments were performed for each material. Measurements determining the hydraulic conductivity at unsaturated through saturated water content were executed using the Unsaturated Flow Apparatus (UFA). The materials tested were North Carolina phosphate rock (NC apatite); reagent grade hydroxyapatite; bone char; a clean, processed quartz sand; Soda Springs phosphate rock; and fish debris. Ash Meadows clinoptilolite was also tested since it is currently being considered for use as a permeable barrier at N-Springs.				
14. SUBJECT TERMS Strontium-90, Groundwater contamination, Phosphates, Chromium, SERDP			15. NUMBER OF PAGES 30	
			16. PRICE CODE N/A	
17. SECURITY CLASSIFICATION OF REPORT unclass.	18. SECURITY CLASSIFICATION OF THIS PAGE unclass.	19. SECURITY CLASSIFICATION OF ABSTRACT unclass.	20. LIMITATION OF ABSTRACT UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

DTIC QUALITY INSPECTED 1

BHI-00857

Rev. 0

Permeable Barrier Materials for Strontium Immobilization:

- UFA Determination of
Hydraulic Conductivity**
- Column Sorption
Experiments**



Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Bechtel Hanford, Inc.
Richland, Washington

For ERC Review

BHI-00857
REV: 0
OU: N/A
TSD: N/A
ERA: N/A

APPROVAL PAGE

Title of Document: Permeable Barrier Materials for Strontium Immobilization:
— UFA Determination of Hydraulic Conductivity
— Column Sorption Experiments

Author(s): T. E. Moody
CH2M HILL Hanford, Inc.

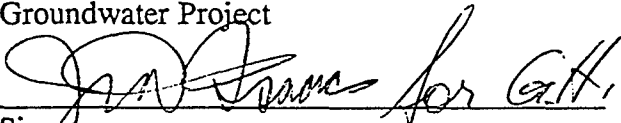
J. Conca
Northwest Environmental Services Testing and Training

Approval: J. D. Isaacs, Groundwater Project Engineer


Signature

7-20-96
Date

G. C. Henckel, Manager
Groundwater Project


Signature

7-20-96
Date

The approval signature on this page indicates that this document has been authorized for issue to U.S. Department of Energy, Richland Operations Office through appropriate channels. No other forms or signatures are required to document this information release.

BHI-DIS 9-23-96 *MM*

EXECUTIVE SUMMARY

Selected materials were tested to emulate a permeable barrier and to examine the (1) capture efficiency of these materials relating to the immobilization of strontium-90 (Sr^{90}) and hexavalent chromium (Cr^{6+}) in Hanford groundwater and (2) hydraulic conductivity of the barrier material relative to the surrounding area. The emplacement method investigated was a permeable reactive barrier to treat contaminated groundwater as it passes through the barrier. The hydraulic conductivity function was measured for each material, and retardation column experiments were performed for each material. Measurements determining the hydraulic conductivity at unsaturated through saturated water content were executed using the Unsaturated Flow Apparatus (UFA). The materials tested were North Carolina phosphate rock (NC apatite); reagent grade hydroxyapatite; bone char; a clean, processed quartz sand (for mixing to increase permeability of reactive barrier); Soda Springs phosphate rock; and fish debris. Ash Meadows Clinoptilolite was also tested since it is currently being considered for use as a permeable barrier at N-Springs. The materials were ranked according to hydraulic conductivity (permeability relative to water) as follows:

bone char > quartz sand > NC apatite >> fish debris:sand $\approx$ Ash Meadows clinoptilolite:sand >> clinoptilolite >> hydroxyapatite > Soda Springs phosphate rock > fish debris

Retardation column studies were conducted using 100-micrograms per milliliter ($\mu\text{g/mL}$) Cr^{6+} solutions. The NC apatite, pure hydroxyapatite, and apatitic fish debris were tested for ability to immobilize Cr^{6+} in solution. All three materials were ineffective. However, when the NC apatite was mixed with a reductant, hydroxylamine sulfate, at 10 percent by weight, the Cr^{6+} was reduced and effectively immobilized. The resultant effluent was measured at $<1 \mu\text{g/mL}$ total chromium. The effluent sulfate concentration increased to $1,600 \mu\text{g/mL}$, evidence of the release of sulfate from the hydroxylamine during the reduction of Cr^{6+} . Oxidation of the effluent using a peroxide (Na_2O_2) produced no measurable Cr^{6+} , indicating the reduced chromium was immobilized. Since NC apatite, hydroxyapatite, and apatitic fish debris were ineffective in

immobilizing Cr^{6+} without the use of reductant, the remainder of the testing was targeted at immobilizing strontium (Sr).

The selected test materials exhibited variable efficiency for the immobilization of 500 $\mu\text{g/mL}$ Sr in Hanford groundwater under field conditions. Natural apatites have high concentrations of Sr. Because of the Sr in the apatite structure, these materials do not effectively immobilize the Sr in solution. Retardation factors (R_f), equal to the ratio of the velocities of the groundwater and the contaminant species ($R_f = V_{\text{gw}}/V_{\text{sp}}$), were experimentally measured, for

- Ash Meadows clinoptilolite, $R_f = 132$
- NC apatite, $R_f = 45$
- bone char, $R_f = 30.1$
- fish debris, $R_f = 45$.

The Soda Springs phosphate rock and the hydroxyapatite had very low permeability and did not conduct any fluid over the experimental time period. Therefore, they were rejected as reasonable barrier materials.

Batch tests on the test materials using the spiked groundwater solution gave very different results for some materials. Synthetic Hanford groundwater was spiked with 500 $\mu\text{g/mL}$ Sr. The distribution coefficients, K_d , were calculated from the results and used to estimate R_f for

- bone char, $R_f = 1,444$
- Ash Meadows clinoptilolite, $R_f = 667$
- sand, $R_f = 83.3$
- Soda Springs phosphate rock, $R_f = 78.2$
- NC apatite, $R_f = 45.2$
- fish debris, $R_f = 44.7$.

The Ash Meadows clinoptilolite and the bone char showed greatly increased R_f because the batch tests were run for 24 hours and were continuously shaken, allowing complete interactions and final conditions closer to chemical equilibrium. In an actual permeable-barrier field situation, the residence time is only one hour or less. Good contact and complete interactions are not possible for some materials, and the actual R_f will be much lower than estimated from batch studies.

Under these conditions, the bone char and the Ash Meadows clinoptilolite are highly affected by residence time while the apatites are not.

BHI-00857

Rev. 0

CONTENTS

1.0	INTRODUCTION	1-1
2.0	BACKGROUND AND PREVIOUS RESULTS	2-1
2.1	BUNKER HILL MINING SITE APATITE REMEDIATION FEASIBILITY STUDY	2-1
3.0	EXPERIMENTAL METHODS	3-1
3.1	HYDRAULIC CONDUCTIVITY AND BARRIER PERMEABILITY	3-1
3.2	RETARDATION AND SORPTION	3-2
4.0	RESULTS	4-1
4.1	HYDRAULIC CONDUCTIVITY AND BARRIER PERMEABILITY	4-1
4.2	RETARDATION AND SORPTION	4-1
5.0	REFERENCES	5-1

FIGURES

2-1.	Bunker Hill Soil Sorption Results	2-3
3-1.	Unsaturated Flow Apparatus Rotor and Seal Assembly	3-4
3-2.	Configuration for Column Flow Experiments	3-5
4-1.	Hydraulic Conductivity of Preferred Phosphate Barrier Materials	4-4
4-2.	Hydraulic Conductivity of Unacceptable Phosphate Barrier Materials	4-5
4-3.	Hydraulic Conductivity of Ash Meadows Clinoptilolite	4-6
4-4.	Breakthrough Curves for Strontium at 5.0 mL/hr Flow Rate	4-7
4-5.	Breakthrough Curves for Strontium at 0.5 mL/hr Flow Rate	4-8

TABLES

4-1.	Hydraulic Conductivity Values Determined Using the UFA	4-9
4-2.	Strontium Column Breakthrough Values for the Candidate Barrier Materials	4-10
4-3.	Strontium Batch Tests for the Candidate Barrier Materials	4-11

ACRONYMS

cm/s	centimeters per second
cm ²	square centimeter
cm ³	cubic centimeters
EPA	U.S. Environmental Protection Agency
g	gram
ICP-MS	inductively coupled plasma mass spectrometry
mg/kg	milligrams per kilogram
mL/h	milliliters per hour
NC apatite	North Carolina phosphate rock
NESTT	Northwest Environmental Services Testing and Training
ppm	parts per million
rpm	rotations per minute
UFA	Unsaturated Flow Apparatus
°C	degrees Celsius
μg/mL	micrograms per milliliter

1.0 INTRODUCTION

The problem of contaminant metals in soils and groundwater is presently identified by the U.S. Environmental Protection Agency (EPA) as one of the most critical environmental risks. Metals readily leach from contaminated soils and sediments and serve as a constant source of metal contamination to groundwater. This work investigated the stabilization of strontium (Sr) and oxidized chromium by chemical interactions with calcium-phosphate materials and Ash Meadows clinoptilolite in permeable barriers. The objective of this work was to determine how well specific metals are immobilized by calcium-phosphate materials, the capacity and efficiency of these minerals relative to the inventory of metal contaminants, and the hydraulic conductivity of each material relative to the environmental conditions of interest. Specifically, this project addresses the groundwater at the Hanford Site in Washington State that has high levels of Sr contamination and may be amenable to calcium-phosphate stabilization.

An important aspect of this treatment is that the metal stabilization, if incurred by calcium-phosphate materials, is nearly irreversible. It is not a simple sorption that can later desorb, it is not a reduction that can later oxidize, and it is not a mineral phase that can later leach. Metals sequestered in these materials have great durability and leach resistance that significantly exceed other chemically stabilized waste forms. The mineral structure is very stable over a wide range of environmental conditions (e.g., pH 2.5 to 13.5, to temperatures up to hundreds of degrees Celsius [$^{\circ}\text{C}$]) in the presence of aqueous- and nonaqueous-phase liquids; in fresh water and in brines; and under disruptions such as earthquakes, ground subsidence, or human intrusion for geologically long time periods (i.e., hundreds of millions of years). Therefore, the metals will no longer be a source for further groundwater contamination. Also, because of this extreme stability, the effects of gravity, soil heterogeneity, hydrology, and other properties of the subsurface do not affect the performance, and, they, themselves, are not affected by this treatment.

When it occurs, the reaction between certain apatites and metal is rapid (Ma et al., 1993; Moody and Wright, 1995), so the treatment is effective immediately, requiring no time for the material to precipitate the contaminant metal. Previous results indicate that the North Carolina phosphate rock (NC apatite) can sequester well over 20 percent of its weight in metals, perhaps as much as 40 percent for ideal metals. Remediation technologies for other contaminants are not inhibited by this treatment (e.g., metal stabilization by phosphate treatment will not affect vapor stripping or bioremediation of organics from the same soils in a mixed-waste system). While calcium phosphate treatments provide some phosphate nutrients for subsurface microbial populations, the solubilities are so low that eutrophication and other phosphate-loading problems that occur with organophosphates do not occur. Phosphate stabilization is possible using existing technologies for emplacement. Also, performance depends upon the initial calcium phosphate selected. Not all are equally reactive or efficient. The ultimate goal of this study is an applied demonstration of the performance using actual groundwater and metal contaminants.

BHI-00857

Rev. 0

2.0 BACKGROUND AND PREVIOUS RESULTS

The groundwork for this research has been laid by previous studies in widely divergent disciplines, including (1) phosphate mineralogy and crystal chemistry (Skinner, 1987 and 1989; Skinner and Burnham, 1968; Wright, 1990a and b; Wright et al., 1990); (2) scavenging and sequestration of minor and trace elements, such as uranium, metals, and the rare earth elements, in natural phosphate deposits (McArthur et al., 1990); (3) remediation studies of phosphate/lead systems (Ma et al., 1993; Ruby et al., 1994; Xu and Schwartz, 1994; Stanforth and Chowdhury, 1994; Davis et al., 1992); (4) the impact and accessibility of phosphorus fertilizers to crops (Adepoju et al., 1986); (5) natural analogues in metallic mineral deposits (Koeppenkastrop and De Carlo, 1988, 1990; De Carlo, 1990); (6) phosphate diagenesis during the formation and evolution of phosphorite deposits (McArthur, 1985); and, (7) the evidence of changes in the paleochemical evolution of oceans, atmospheres, and climates evidenced by metals, particularly Sr, lanthanides, and actinides incorporated into fossil teeth that have an apatite composition (Wright, 1990a and b). Results demonstrate that stabilization of contaminated soils and groundwater by apatite has the potential to be the most successful and widely applicable remediation strategy for metals and radionuclides in the foreseeable future.

Apatite minerals form naturally and are stable across a wide range of geologic conditions for hundreds of millions of years (Nriagu, 1974; Wright, 1990). Wright, Conca, and others (Wright et al., 1987a, 1990; Burke et al., 1982) investigated the trace element composition of apatite in fossil teeth and bones and in sedimentary phosphorite deposits through geologic time. They found that apatite deposited in seawater concentrates metals and radionuclides from the seawater to millions of times the ambient concentration and locks them into the apatite structure for up to a billion years with no subsequent desorption, leaching, or exchange even after extreme diagenetic changes in the pore water chemistry and pH, extreme temperatures, and geologic or tectonic disruptions. By contrast, metals stabilized or taken out of solution as a function of ion exchange are much more susceptible in being desorbed under these conditions. Depending on specific conditions, the relative stabilities of apatites and the other test materials in the natural environment under subsurface geologic diagenetic conditions based on solubility constants (Garrels and Christ, 1965; Stumm and Morgan, 1981) are as follows:

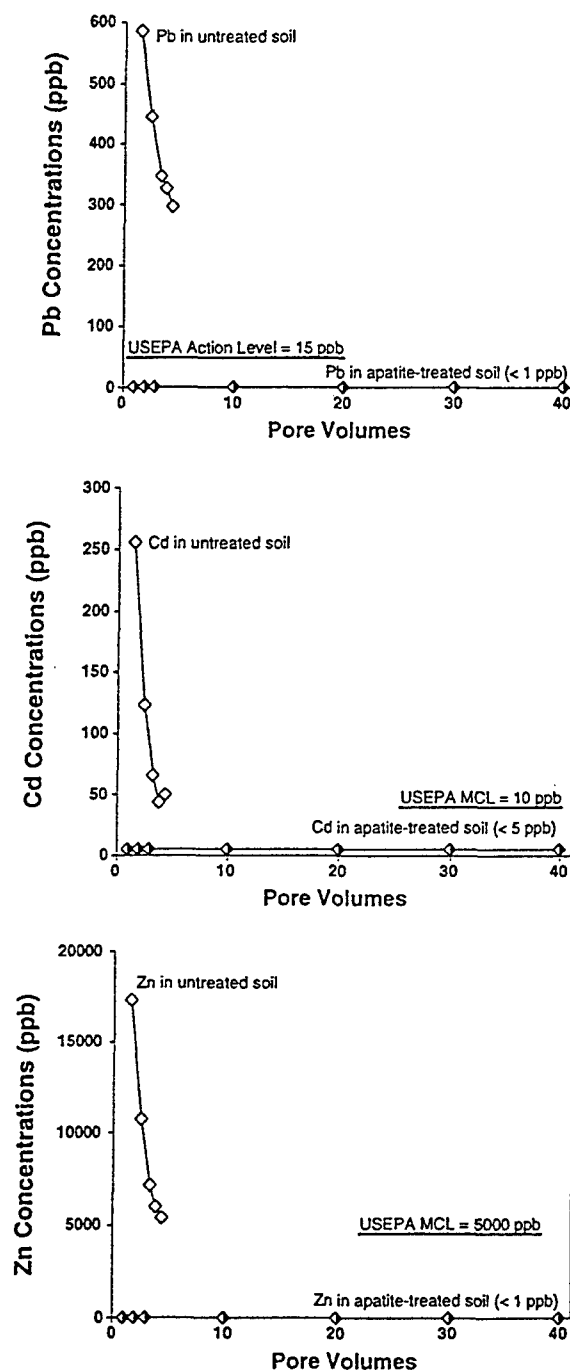
apatite ($K_{sp} > 20$) $\gg$ quartz ($K_{sp} \approx 4$) $>$ zeolite ($K_{sp} < 4$).

2.1 BUNKER HILL MINING SITE APATITE REMEDIATION FEASIBILITY STUDY

Northwest Environmental Services Testing and Training (NESTT) and the Westinghouse Hanford Company research group recently investigated the metal-stabilization potential of reactive phosphates mined from phosphorite deposits, obtained from fish cannery wastes, and produced as reagent-grade calcium triphosphate. Preliminary studies used the mine tailings and soils from the Bunker Hill Mining District in Idaho, which contain 1,000 to 4,000 milligrams per kilogram (mg/kg) (ppm), or 0.1 to 0.4 percent by weight, of lead (Pb), as well as high

concentrations of zinc (Zn) and cadmium (Cd). Data from the chemical and mineralogical speciation studies and batch tests were used in the geochemical code MINTEQA2 (Allison et al., 1991) to determine the stability relationships of the soil and metal-apatite minerals under varying conditions. The metal-apatite phases were predicted to be the most stable under all expected subsurface conditions (Moody and Wright, 1995). Soil-column experiments were then carried out to test the performance of the untreated and apatite-treated soils. Results showed that leachates from untreated Bunker Hill soils were in the hundreds to thousands of mg/kg (ppm) range for Pb and Zn, well in excess of the drinking water standards. Cadmium was hundreds of mg/kg (ppm), also well in excess of the drinking water standards. However, leachates from apatite-treated Bunker Hill soils showed concentrations for Pb, Zn, and Cd below the detection limits of 1 $\mu\text{g/kg}$ using inductively coupled plasma mass spectrometry (ICP-MS) (Figure 2-1). These concentrations are well below drinking water limits. The same performance occurred whether the apatite was mixed into the soil, as in auguring, or placed as a layer downgradient of the contaminated soil, as a permeable reactive barrier, or used in an aboveground treatment system.

Figure 2-1. Bunker Hill Soil Sorption Results



Soil column test desorption/sorption run on Bunker Hill soil with only 1-percent apatite by weight using vadose-zone water at a recharge of 2×10^{-7} centimeters per second (cm/s). Initial leachate from untreated soils showed metal concentrations well above regulatory levels. Apatite-treated soils showed concentrations below ICP-MS detection limits.

3.0 EXPERIMENTAL METHODS

3.1 HYDRAULIC CONDUCTIVITY AND BARRIER PERMEABILITY

The permeability of barrier materials will be affected by changes in flow rates and water-table levels. The single most important physical transport property is the permeability relative to water, called the hydraulic conductivity, K , which is a strong, nonlinear function of the volumetric water content, θ . Traditional methods of investigating flow systems require very long times because normal gravity does not provide a large enough driving force relative to the low hydraulic conductivities that characterize saturated to unsaturated conditions. Pressure techniques often bypass portions of the sample because pressure is not a whole body force like gravity and will seek the path of least resistance (e.g., fractures, sandy areas, and macropores) and can affect the stabilities of common minerals like calcite, clays, and gypsum. To solve these problems, an unsaturated flow apparatus (UFA) was developed based on open-flow centrifugation (Figure 3-1). A hydraulic steady state is achieved in hours in any porous media even at very low water contents by using an adjustable, whole-body driving force in combination with precision fluid flow (Conca and Wright, 1992). The UFA is actually a Darcy's Law machine in that the operator adjusts both the flux and the driving force and attains any desired hydraulic steady state. The normal operating range is from saturated down to 10^{-11} cm/s (10^{-8} Darcy; 10^{-16} square centimeters [cm^2]) or 10^{-14} cm/s for only saturated conditions. Temperature can be controlled from -20°C to 150°C . Sample sizes can range from less than 40 cubic centimeter (cm^3) cores to Shelby tube-sized samples (280 cm^3). The UFA isolates and separates advection from other processes (e.g., diffusion or vapor flow), allowing precise measurement of the residual water content. The UFA instrument consists of an open-flow ultracentrifuge with constant, ultralow flow pumps that provide fluid to the sample surface through a rotating seal assembly and microdispersal system. Effluent is collected in a transparent, volumetrically calibrated chamber, which is observed during operation using a strobe light. The UFA method is effective because it allows the operator to set the variables in Darcy's Law under which the fluid flux equals the hydraulic conductivity times the fluid driving force. Under a centripetal acceleration in which water is driven by both the matric potential gradient and the centrifugal force per unit volume, Darcy's Law is as follows:

$$q = -K(\psi) [d\psi/dr - \rho\omega^2r] \quad (1)$$

where

- q = the flux density into the sample
- K = the hydraulic conductivity
- ψ = the matric potential
- $d\psi/dr$ = the matric gradient
- $\rho\omega^2r$ = the centrifugal force per unit volume
- r = the radius from the axis of rotation
- ρ = the fluid density
- ω = the rotation speed in radians per second.

Above speeds of about 300 rpm, if sufficient flux density exists, $d\psi/dr \ll \rho\omega^2r$. Rearranging the equation and expressing hydraulic conductivity as a function of volumetric water content, θ , Darcy's Law becomes

$$K(\theta) = q/\rho\omega^2r \quad (2)$$

As an example, a silt from the Hanford formation accelerated to 2,500 rpm with a flow rate of 0.01 milliliter per hour (mL/h) reached hydraulic steady state in 10 hours at a target volumetric water content of 16.4 percent and an unsaturated hydraulic conductivity of 4×10^{-10} cm/s. Because of the ability to control the flow rate (± 1 percent nonpulsating), rotation speed (± 5 rotations per minute [rpm]) and weight measurement (± 0.001 gram [g]), hydraulic conductivity is known to within ± 8 percent at a volumetric water content known to within ± 2 percent (Nimmo et al., 1994).

Comparisons between the UFA method, soil columns, van Genuchten/Mualem estimations, and lysimeter measurements on the same materials show excellent agreement (Nimmo et al., 1994; Conca and Wright, 1992). Compaction from acceleration is negligible for soils and sediments at or near their field densities. Three-dimensional deviations of the driving force with position in the sample are less than a factor of two, and water distribution is uniform in homogeneous samples. Heterogeneous samples can have more than one component (e.g., a silt lens in a coarse sand, a fractured rock with matrix porosity, or a gravel with porosity internal to the gravel particles). In the field, each component of a heterogeneous sample reaches its own steady-state condition under the whole-body force of gravity. To reproduce the field behavior in the laboratory also requires a whole-body force. Pressure techniques are not appropriate as pressure is a surface force that acts through the component of least resistance. However, the UFA method uses the whole-body force of an acceleration and allows heterogeneous samples to be successfully run in the laboratory.

3.2 RETARDATION AND SORPTION

Chemical experimental methods consisted of retardation-column flow experiments and batch experiments. Retardation factors can be determined in flow experiments where R_f for a particular species is the ratio of the solution velocity to the species velocity. The retardation factor for that species is given by Bouwer (1991):

$$R_f = V_{gw}/V_{sp} = 1 + \rho K_d/n \quad (3)$$

where

- V_{gw} = the velocity of carrier fluid
- V_{sp} = the velocity of the species
- ρ = the dry bulk density
- n = the porosity.

The K_d is defined as the moles of the species per gram of solid divided by the moles of the species per milliliter of solution.

If none of a particular species is lost to the solid phase, then $K_d = 0$ and $R_r = 1$ for that species. In column experiments, a breakthrough curve is obtained for the particular species, and R_r is determined as the pore volume at which $C/C_0 = 0.5$. It is now generally assumed that for unsaturated systems $n = \theta$ where θ is the volumetric water content (Bouwer, 1991; Conca and Wright, 1992b). Figure 3-2 shows the experimental configuration for the flow columns. Columns were plastic chromatographic columns filled with approximately 5 g of each material. In testing the treatment efficacy of calcium-phosphate materials for immobilization of Cr^{6+} , a concentration of $100 \mu\text{g/mL}$ Cr^{6+} was pumped into the materials at 5 mL/hr. Hanford groundwater, spiked with $500 \mu\text{g/mL}$ Sr, was pumped into the columns at two different rates, 5 mL/hr and 0.5 mL/hr. Effluent was collected at selected times and analyzed for Sr and Cr^{6+} using ICP-MS and colorimetric methods, respectively.

Figure 3-1. Unsaturated Flow Apparatus Rotor and Seal Assembly

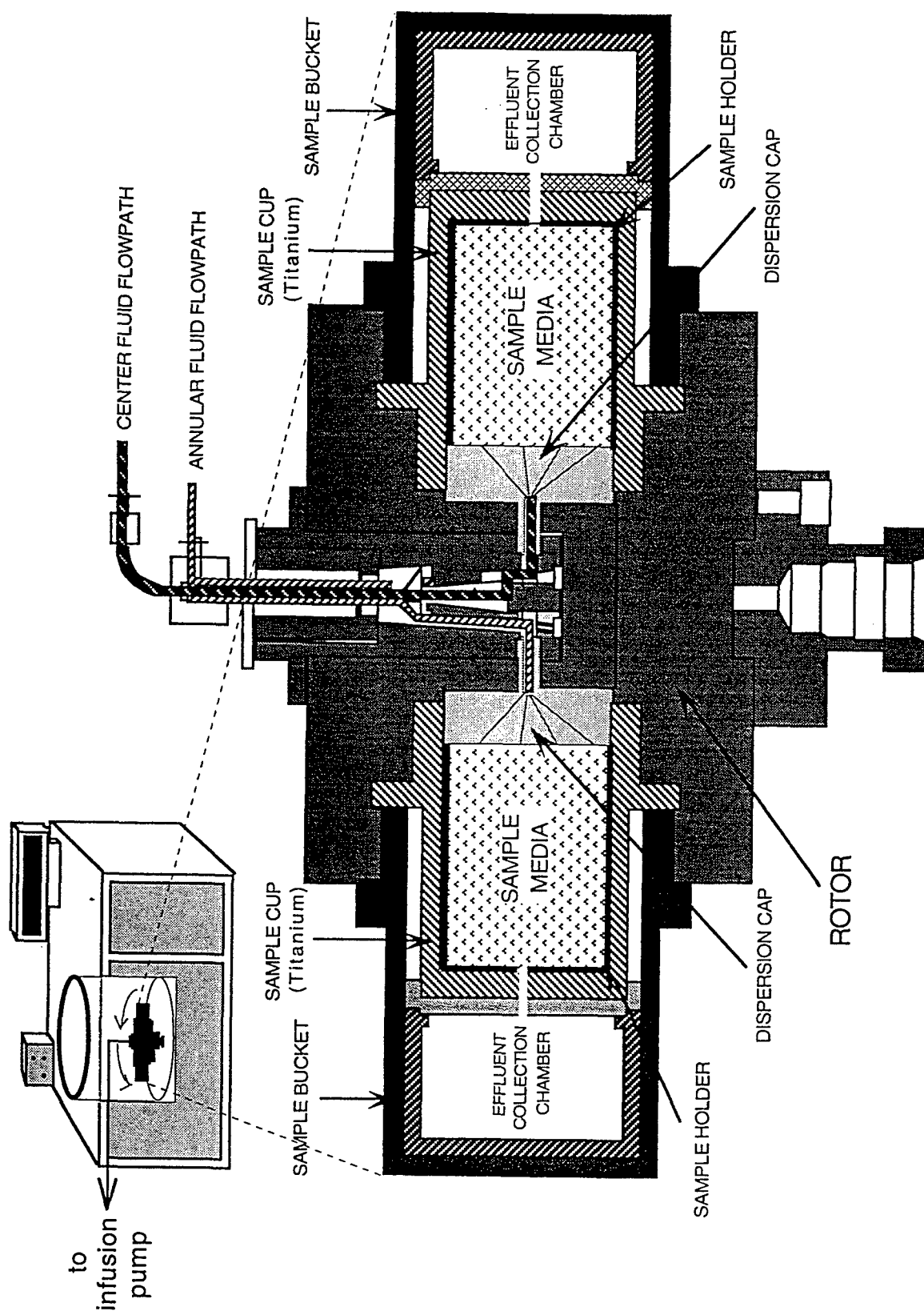
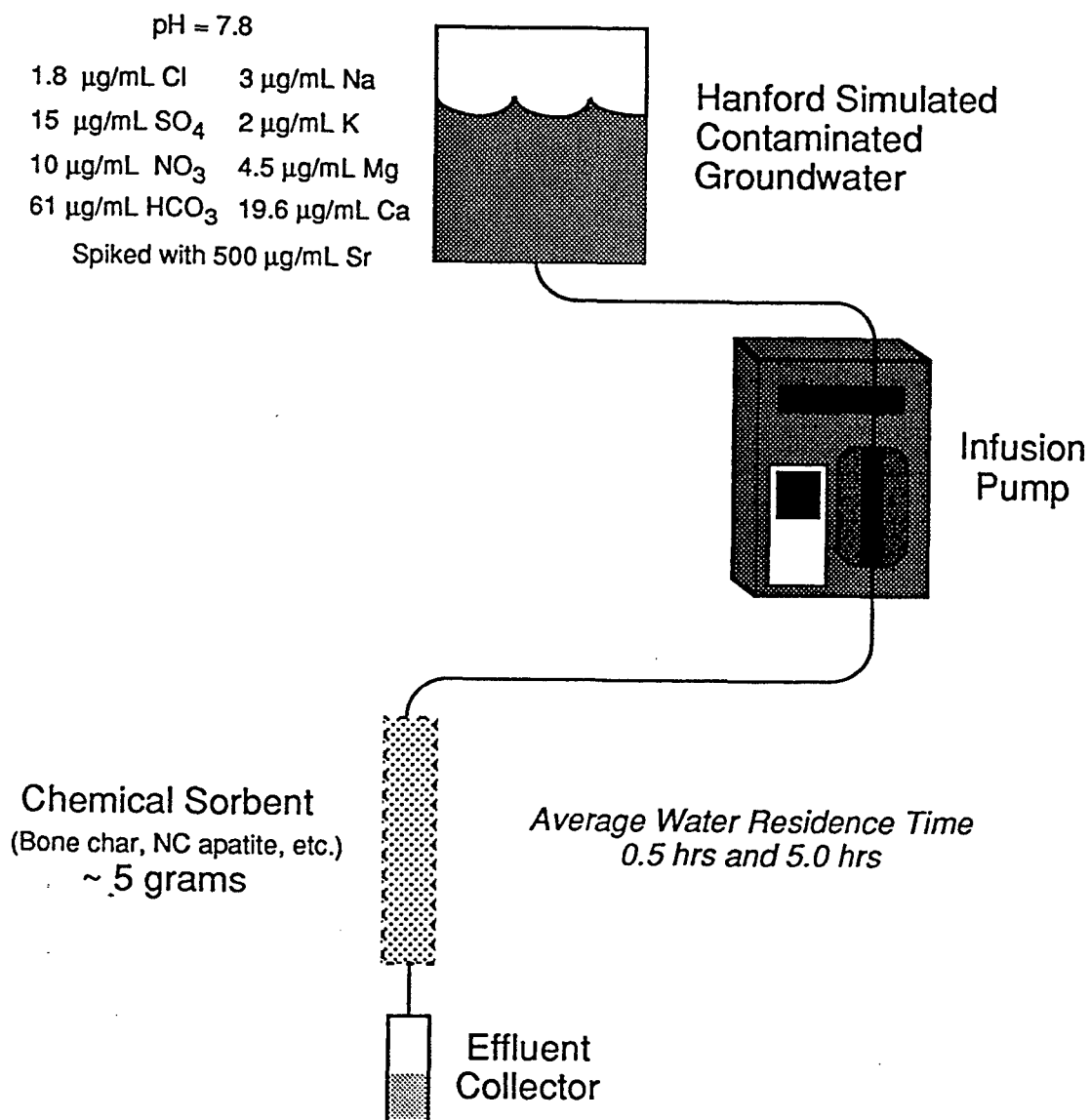


Figure 3-2. Configuration for Column Flow Experiments —



BHI-00857

Rev. 0

4.0 RESULTS

4.1 HYDRAULIC CONDUCTIVITY AND BARRIER PERMEABILITY

A permeable reactive barrier requires an appropriate hydraulic conductivity in the field relative to the material upgradient of the barrier. If the barrier material has a lower permeability than the upgradient soil, the groundwater flow will be restricted and will back up and flow around or over the barrier and thus avoid the treatment system. If the barrier material has a much higher permeability than the upgradient soil, unusual flow paths may develop, the residence time of the groundwater may be too low for complete treatment, and the surface area of reaction may be too low for efficient reaction. Because the groundwater level can fluctuate at the Hanford Site, it is important to obtain hydraulic conductivity values at unsaturated through saturated water content. The unsaturated conductivity curve also indicates the effective pore-size distribution and the susceptibility to clogging up and silting the barrier.

Figures 4-1 through 4-3 show the permeability results for the candidate barrier materials. The data for these figures are presented in Table 4-1. Also shown in each figure is the curve for Hanford soil upgradient of the barrier. A prominent shelf in the curve shown by all the materials in Figure 4-1 indicates a well sorted pore-size distribution. The saturated permeability of the bone char is similar to that of the Hanford soil, and the NC apatite is slightly lower. Obtaining hydraulic conductivity data for fish debris proved very difficult because water would not flow through this material. Therefore, no data are presented for this material. The fish debris, even when mixed with clean sand, is significantly lower and may not be acceptable. The hydroxyapatite and Soda Springs phosphate rock shown in Figure 4-2 both have much lower saturated permeabilities and are poorly sorted, making them unacceptable barrier materials. The pure Ash Meadows clinoptilolite sample shown in Figure 4-3 has a very irregular and nonreproducible hydraulic behavior, especially at the saturated end. Mixing the clinoptilolite with clean quartz sand in a 50:50 ratio makes the clinoptilolite behave more regularly and provides a stable, saturated hydraulic conductivity that is reasonable for a barrier material. Further studies are being done for larger particle-size clinoptilolite proposed for the N-Springs barrier field demonstration. These results will be presented in a forthcoming report.

4.2 RETARDATION AND SORPTION

Retardation column studies were executed using 100 $\mu\text{g/mL}$ Cr^{6+} solutions. The NC apatite, pure hydroxyapatite, and apatitic fish debris were run and shown to be completely ineffective in immobilizing the Cr^{6+} in solution. However, when the NC apatite was mixed with a reductant, hydroxylamine sulfate, at 10 percent by weight, the Cr^{6+} was reduced and effectively immobilized. The resultant effluent was measured at less than 1 $\mu\text{g/mL}$ total chromium. The effluent-sulfate concentration increased to 1,600 $\mu\text{g/mL}$, evidence of the release of sulfate from the hydroxylamine during the reduction of Cr^{6+} . Oxidation of the effluent using a peroxide (Na_2O_2) produced no measurable Cr^{6+} , indicating the reduced chromium was immobilized. Since

the NC apatite, hydroxyapatite, and apatitic fish debris were ineffective in immobilizing Cr^{6+} , the remainder of the testing was targeted at immobilizing Sr.

For Sr sorption and breakthrough, the experiments were run and the effluents collected for analysis at a later time. Because of previous results in other systems, it was expected that a breakthrough would take several weeks. However, in these systems, it was found that the breakthrough occurred quickly, so the breakthrough curves did not show much detail. The retardation factor was relatively low for each material (Figure 4-4). The data for Figure 4-4 are presented in Table 4-2. The retardation factor for each material is as follows:

- Ash Meadows clinoptilolite, $R_f = 132$
- NC apatite, $R_f = 45$
- bone char, $R_f = 30.1$
- fish debris, $R_f = 45$.

The Soda Springs phosphate rock and the hydroxyapatite were so impermeable that they did not conduct any fluid over the experimental time period and so were rejected as reasonable barrier materials. The fish debris began to conduct but, after the first effluent collection, also became relatively impermeable, and the run was stopped. Note that this first point for the fish debris lies exactly along the line for the NC apatite in Figure 4-4, indicating similar behavior described in previous studies (Moody and Wright, 1995; Wright et al., 1995). This experiment was run with a flow rate of 5 mL/hr to give a residence time of about 0.5 hours in the sample. The 5 mL/hr flow rate is equivalent to a groundwater flow rate of 42.7 meters/day. This gives a residence time of 0.5 hours in a 3 ft thick barrier.

To decide if residence time was the reason that a breakthrough occurred much more rapidly than anticipated, the residence time was increased to 5 hours by decreasing the flow rate to 0.5 mL/hr (Figure 4-5). The data for Figure 4-5 are presented in Table 4-2. A breakthrough still occurred quickly for the apatites, so the breakthrough curves do not show any more detail. The retardation factor was relatively low for each material except for Ash Meadows clinoptilolite:

- NC apatite, $R_f = 62$
- bone char, $R_f = 48$
- fish debris, $R_f = 54$.

The breakthrough was still rapid for the apatites, although a little higher, suggesting that residence time is not a major factor. The Ash Meadows clinoptilolite had not yet broken through by the time of this writing, and its R_f must be several hundred, more in keeping with the batch tests discussed below.

Batch tests were conducted on the materials to compare with the column studies and to determine if the R_f values are reasonable. Batch tests consisted of 4 g of sample in 40 g of contaminated groundwater shaken at 23°C for 24 hours. Table 4-3 gives the results plus the estimated R_f using Equation 3. The Ash Meadows clinoptilolite and the bone char show greatly increased R_f in the batch tests relative to the column experiments because the batch tests are run for 24 hours and are

vigorously shaken, allowing more complete interactions and final conditions closer to chemical equilibrium, another indication of a residence time effect. In the field, however, the residence time in a permeable barrier situation at Hanford is only an hour or less, and good contact and complete interactions are not possible for some materials, causing the actual R_f to be much lower. The bone char and the Ash Meadows clinoptilolite are highly affected because there is not time for complete diffusion into the particle interiors. The apatites behave similarly between batch and column.

The column experiments, therefore, are a more reliable indication of barrier performance in the field, and Figure 4-1 reasonably describes the behavior of the four candidate materials having adequate hydraulic conductivity to be emplaced as a permeable reactive barrier.

Table 4-3 suggests that the bone char has even better sorption properties than the Ash Meadows clinoptilolite if chemical equilibrium is reached or if the residence time is high enough. Crushing the bone char to a finer grain size would increase its reactivity. Mixing bone char in with Ash Meadows clinoptilolite would improve the hydraulic properties of the clinoptilolite and add the favorable properties of bone char. Likewise, emplacing a thicker barrier would increase the residence time and performance for both clinoptilolite and bone char.

Figure 4-1. Hydraulic Conductivity of Preferred Phosphate Barrier Materials

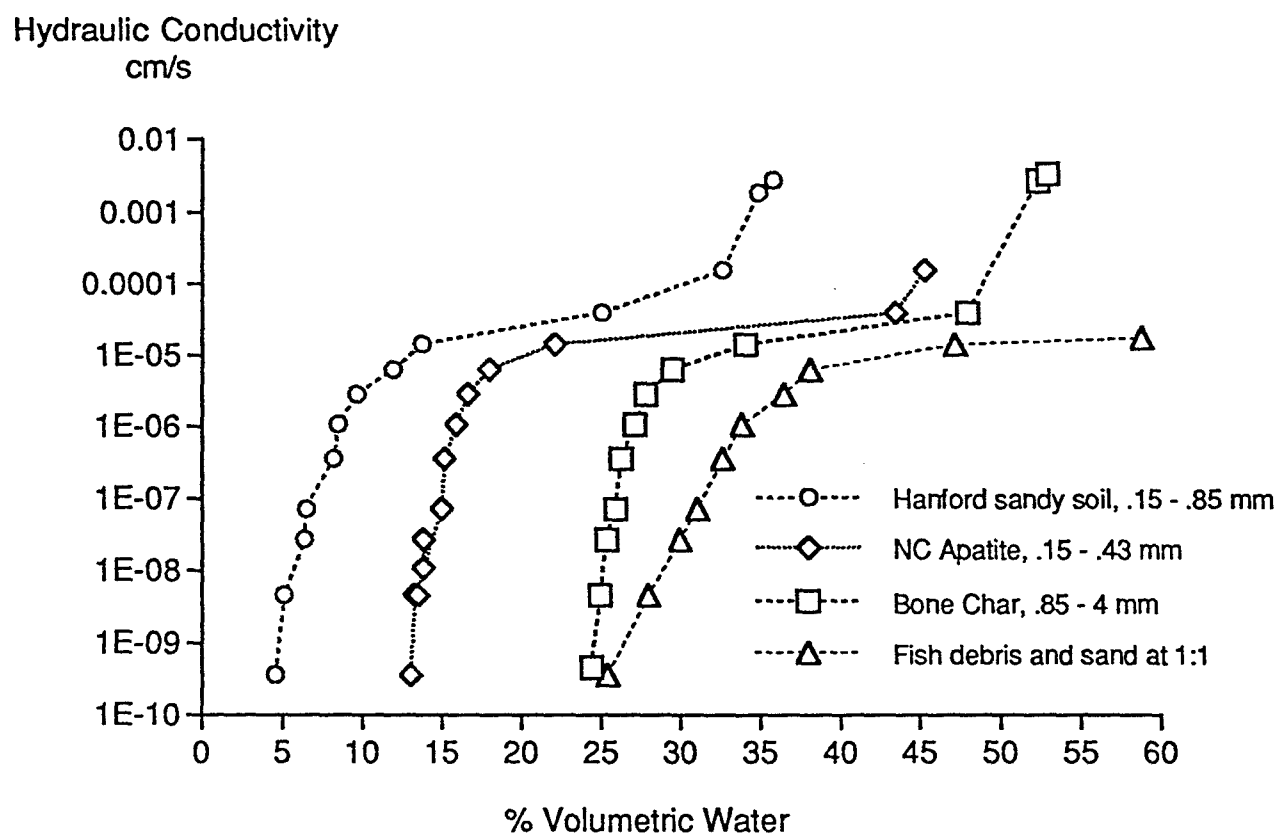


Figure 4-2. Hydraulic Conductivity of Unacceptable Phosphate Barrier Materials

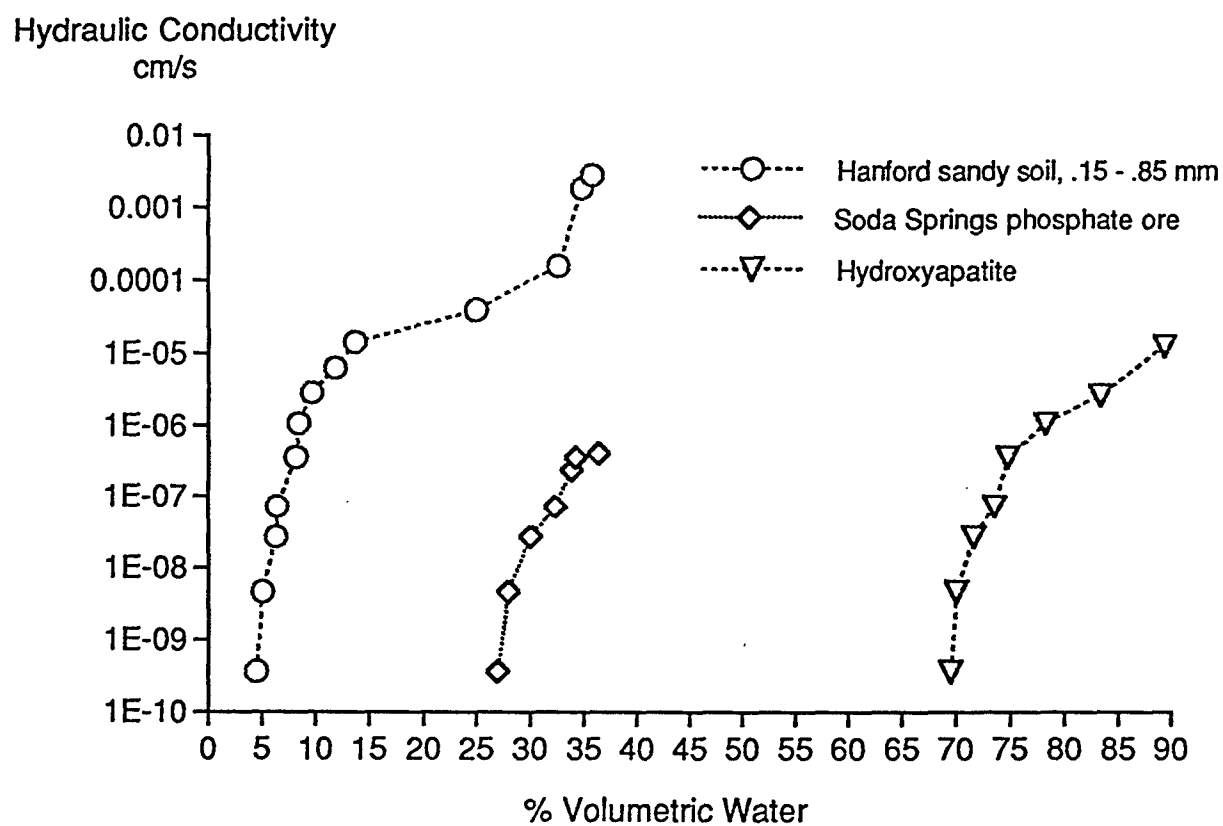


Figure 4-3. Hydraulic Conductivity of Ash Meadows Clinoptilolite

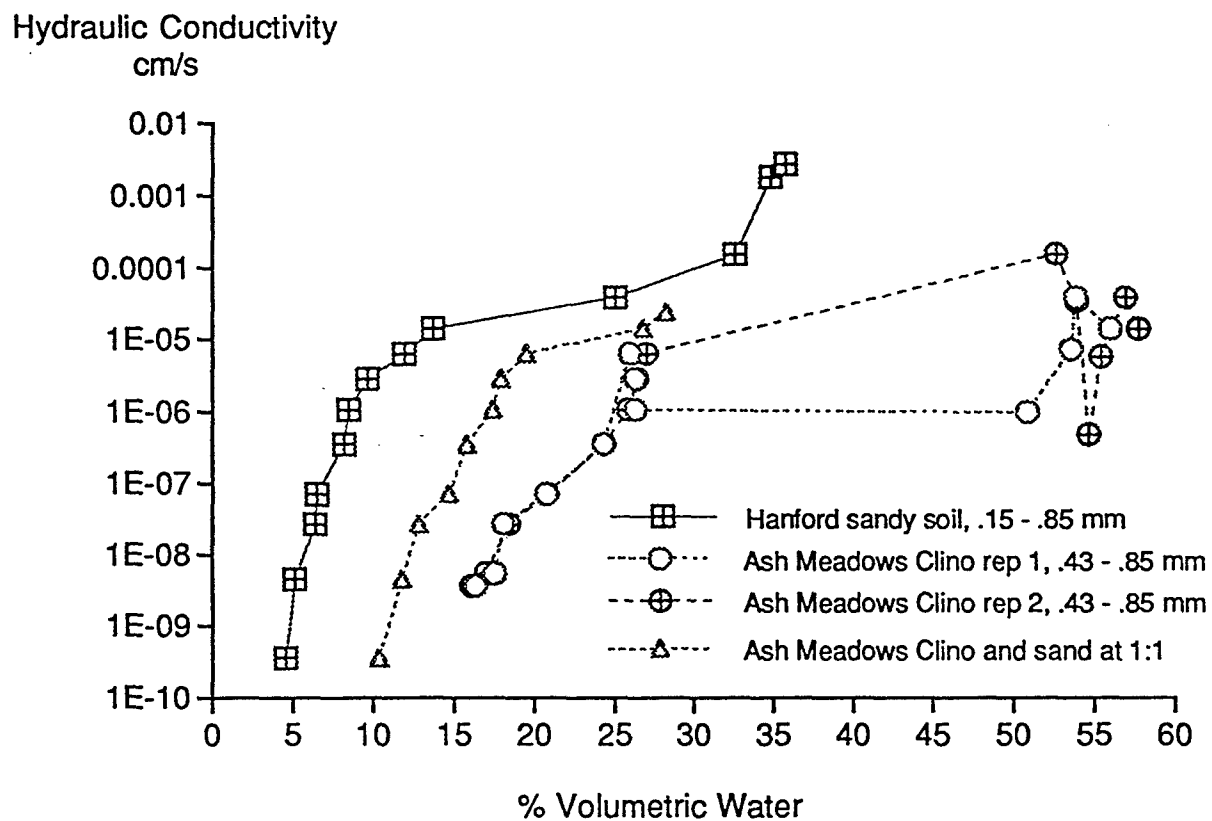


Figure 4-4. Breakthrough Curves for Strontium at 5.0 mL/hr Flow Rate

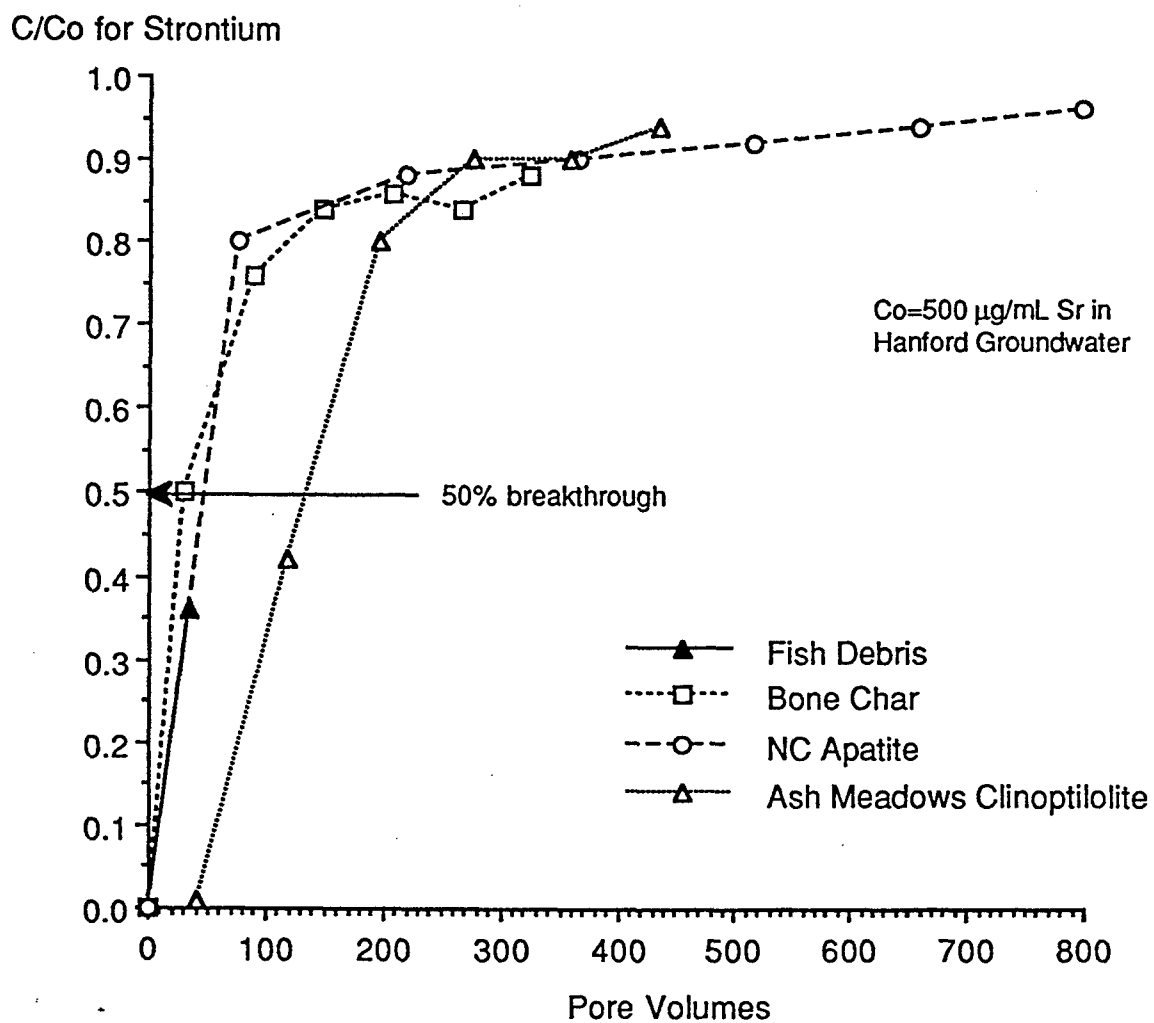


Figure 4-5. Breakthrough Curves for Strontium at 0.5 mL/hr Flow Rate

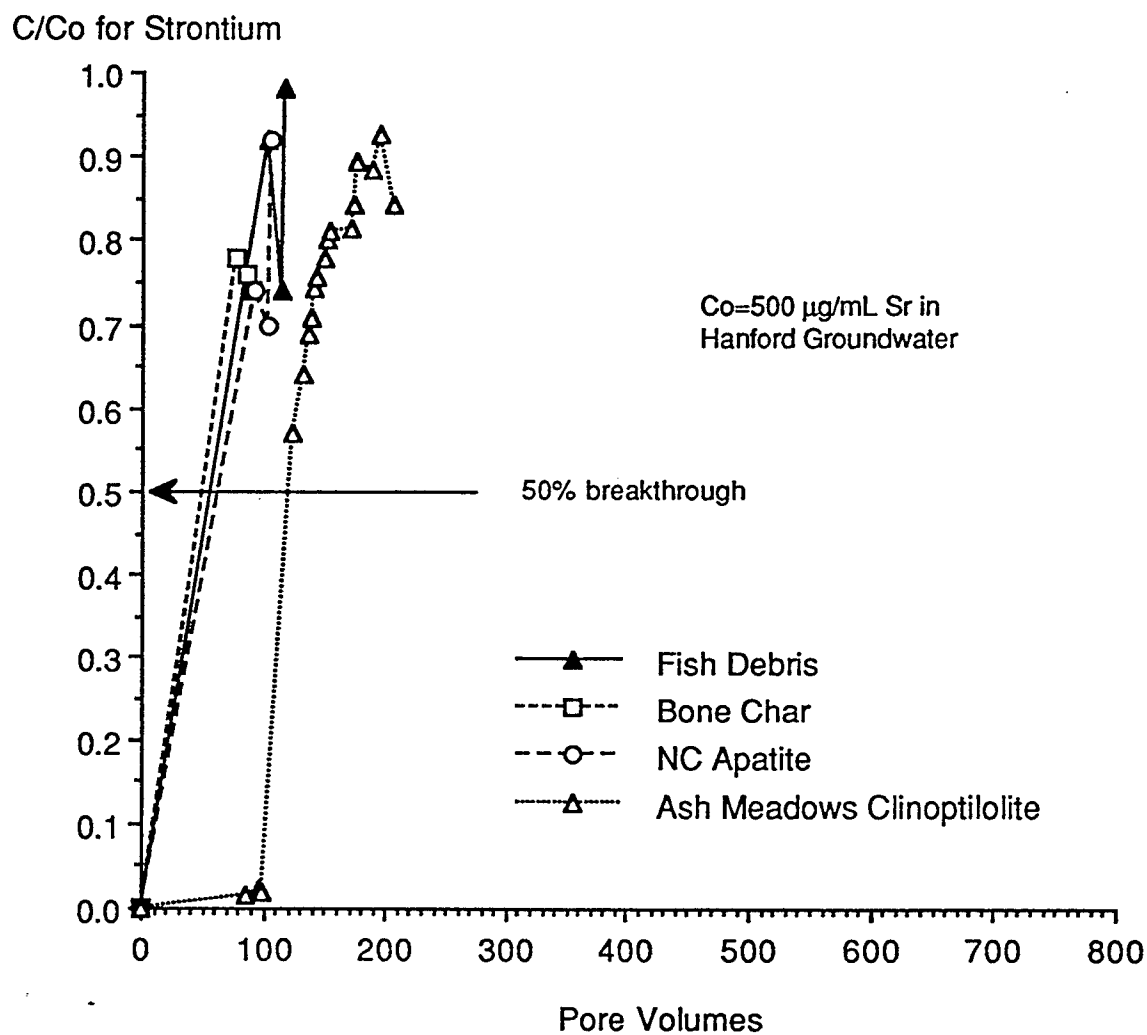


Table 4-1. Hydraulic Conductivity Values Determined Using the UFA^a

Table 4.1. Hydraulic Conductivity Values Determined Using the Unsaturated Flow Apparatus (UFA).

Bone Char		NC Apatite		Hanford Sandy Soil		Ash Meadows Clinoptilolite rep 1		Ash Meadows Clinoptilolite rep 2	
Volumetric Water %	Hydraulic Conductivity cm/s	Volumetric Water %	Hydraulic Conductivity cm/s	Volumetric Water %	Hydraulic Conductivity cm/s	Volumetric Water %	Hydraulic Conductivity cm/s	Volumetric Water %	Hydraulic Conductivity cm/s
52.86	0.00337	45.29	1.58E-04	35.74	2.76E-03	55.43	5.81E-06	50.88	9.93E-07
52.26	0.00271	43.43	3.96E-05	34.83	1.84E-03	53.93	3.47E-05	53.6	7.38E-06
47.88	3.96E-05	22.07	1.43E-05	32.6	1.58E-04	52.69	1.58E-04	53.88	3.96E-05
34.02	1.43E-05	17.98	6.33E-06	25	3.96E-05	56.95	3.96E-05	56.02	1.43E-05
29.4	6.33E-06	16.64	2.85E-06	13.71	1.43E-05	57.76	1.43E-05	25.93	6.33E-06
27.74	2.85E-06	15.9	1.07E-06	11.9	6.33E-06	27	6.33E-06	26.29	2.85E-06
27.05	1.07E-06	15.14	3.56E-07	9.67	2.85E-06	26.43	2.85E-06	26.29	1.07E-06
26.19	3.56E-07	14.95	7.13E-08	8.48	1.07E-06	25.81	1.07E-06	24.29	3.56E-07
25.86	7.13E-08	13.81	2.69E-08	8.21	3.56E-07	24.33	3.56E-07	20.74	7.13E-08
25.29	2.69E-08	13.81	1.08E-08	6.48	7.13E-08	20.79	7.13E-08	18.07	2.69E-08
24.88	4.56E-09	13.48	4.56E-09	6.38	2.69E-08	18.4	2.69E-08	17.52	5.39E-09
24.38	4.56E-10	13.24	4.56E-09	5.1	4.56E-09	16.98	5.39E-09	16.33	3.60E-09
		13	3.60E-10	4.55	3.60E-10	16.07	3.60E-09		
						54.69	4.88E-07		

Hydroxyapatite		Soda Springs Phosphate Ore		Fish Debris and Sand, 1:1		Ash Meadows Clinoptilolite and Sand, 1:1	
Volumetric Water %	Hydraulic Conductivity cm/s	Volumetric Water %	Hydraulic Conductivity cm/s	Volumetric Water %	Hydraulic Conductivity cm/s	Volumetric Water %	Hydraulic Conductivity cm/s
89.36	1.30E-05	36.38	4.02E-07	58.72	1.77E-05		6.32E-06
83.33	2.65E-06	34.23	3.56E-07	47.12	1.43E-05	28.26	2.44E-05
78.29	1.07E-06	33.86	2.37E-07	38.04	6.33E-06	26.76	1.43E-05
74.72	3.56E-07	32.34	7.13E-08	36.43	2.85E-06	19.48	6.33E-06
73.54	7.13E-08	30.05	2.69E-08	33.8	1.07E-06	17.9	2.85E-06
71.62	2.69E-08	27.98	4.56E-09	32.61	3.56E-07	17.38	1.07E-06
70.05	4.56E-09	27.03	3.60E-10	31.02	7.13E-08	15.81	3.56E-07
				29.93	2.69E-08	14.67	7.13E-08
				27.93	4.56E-09	12.81	2.69E-08
				25.38	3.60E-10	11.79	4.56E-09
						10.38	3.60E-10

^aValues presented represent unsaturated through saturated water content.

Table 4-2. Strontium Column Breakthrough Values for the Candidate Barrier Materials

5 mL/hr flow rate

Fish Debris PV = 4.5		Bone Char PV = 4.0		NC Apatite PV = 1.6		Ash Meadows Clinoptilolite PV = 3.0	
Pore Volumes	C/Co	Pore Volumes	C/Co	Pore Volumes	C/Co	Pore Volumes	C/Co
0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3.36E+01	3.60E-01	3.01E+01	5.00E-01	7.43E+01	8.00E-01	4.04E+01	9.60E-03
		8.95E+01	7.60E-01	2.20E+02	8.80E-01	1.19E+02	4.20E-01
		1.48E+02	8.40E-01	3.65E+02	9.00E-01	1.95E+02	8.00E-01
		2.08E+02	8.60E-01	5.15E+02	9.20E-01	2.77E+02	9.00E-01
		2.67E+02	8.40E-01	6.59E+02	9.40E-01	3.58E+02	9.00E-01
		3.24E+02	8.80E-01	7.97E+02	9.60E-01	4.35E+02	9.40E-01

0.5 mL/hr flow rate

Fish Debris + Sand PV = 4.5		Bone Char PV = 4.0		NC Apatite PV = 1.6		Ash Meadows Clinoptilolite PV = 3.0	
Pore Volumes	C/Co	Pore Volumes	C/Co	Pore Volumes	C/Co	Pore Volumes	C/Co
0.00E+00	1.00E-04	0.00E+00	1.00E-04	0.00E+00	1.00E-04	0.00E+00	1.00E-04
1.02E+02	9.20E-01	7.69E+01	7.80E-01	9.16E+01	7.40E-01	8.50E+01	1.60E-02
1.13E+02	7.40E-01	8.63E+01	7.60E-01	1.03E+02	7.00E-01	9.55E+01	2.20E-02
1.16E+02	9.80E-01	8.88E+01	7.40E-01	1.06E+02	9.20E-01	9.84E+01	2.00E-02
						1.23E+02	5.72E-01
						1.32E+02	6.40E-01
						1.35E+02	6.88E-01
						1.38E+02	7.08E-01
						1.41E+02	7.42E-01
						1.43E+02	7.58E-01
						1.49E+02	7.80E-01
						1.52E+02	8.00E-01
						1.54E+02	8.10E-01
						1.70E+02	8.14E-01
						1.73E+02	8.44E-01
						1.75E+02	8.94E-01
						1.90E+02	8.84E-01
						1.95E+02	9.26E-01
						2.07E+02	8.44E-01

Table 4-3. Strontium Batch Tests for the Candidate Barrier Materials

Sample	Distribution Coefficient K_d (milliliter per gram [mL/g])	Bulk Density (gram/milliliter [g/mL])	Porosity (mL/mL)	Retardation Factor (R_f)
Fish debris	19.4	1.35	0.60	44.7
Soda Springs phosphate ore	15.0	1.98	0.38	78.2
NC apatite	12.7	1.60	0.45	45.2
Bone char	823	0.93	0.53	1,444
Ash Meadows clinoptilolite	375	0.96	0.54	667
Hanford sand	13.8	1.81	0.30	83.3

5.0 REFERENCES

- Adepoju, A. Y., P. F. Pratt, and S. V. Mattigod, 1986, "Relationship Between Probable Dominant Phosphate Compound in Soil and Phosphorus Availability to Plants," *Plant and Soil*, Vol. 92, pp. 47-54.
- Allison, J. D., D. S. Brown, and K. J. Novo-Gradac, 1991, *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*, EPA/6003-91/021, U.S. Environmental Protection Agency, Athens, Georgia.
- Bouwer, H., 1991, "Simple Derivation of the Retardation Equation and Application to Preferential Flow and Macrodispersion," *Ground Water*, Vol. 29, pp. 41-46.
- Burke, W. H., R. E. Denison, E. A. Heatherington, R. B. Koepnick, H. F. Nelson, and J. B. Otto, 1982, "Variation of Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic Time," *Geology*, Vol. 10, pp. 516-519.
- Conca, J. L. and J. V. Wright, 1992, "Diffusion and Flow in Gravel, Soil, and Whole Rock," *Applied Hydrogeology*, Vol. 1, pp. 5-24.
- Davis, A., M. V. Ruby, and P. D. Bergstrom, 1992, "Bioavailability of Arsenic and Lead in Soils from the Butte, Montana, Mining District," *Environmental Science and Technology*, Vol. 26, pp. 461-468.
- De Carlo, E. J., 1990, "Paleoimplications of Intrasample Rare Earth Element Variability in A Marine Fe-Mn Crust from the Central Pacific Ocean," *Chemical Geology*.
- Garrels, R. M. and C. L. Christ, 1965, *Solutions, Minerals, and Equilibria*, Freeman, Cooper and Company, San Francisco, CA.
- Koeppenkastrop, D. and E. J. De Carlo, 1988, "Adsorption of Rare Earth Elements from Seawater onto Synthetic Mineral Phases," *EOS Transactions of Amer. Geophysical Union*, Vol. 69, p. 1254.
- Koeppenkastrop, D. and E. J. De Carlo, 1990, "Sorption of Rare Earth Elements from Seawater onto Synthetic Mineral Phases," *Chemical Geology*.
- Ma, Q. Y., S. J. Traina, and T. J. Logan, 1993, "In Situ Lead Immobilization by Apatite," *Environmental Science and Technology*, Vol. 27, pp. 1803-1810.
- McArthur, J. M., 1985, "Francolite Geochemistry -- Compositional Controls on Formation, Diagenesis, Metamorphism, and Weathering," *Geoch. Cosmoch. Acta*, Vol. 49, pp. 23-35.

- McArthur, J. M., A. R. Sahami, M. Thirwall, P. J. Hamilton, and A. O. Osborn, 1990, "Dating Phosphogenesis with Sr^{90} Isotopes," *Geoch. Cosmoch. Acta*, Vol. 54, pp. 1343-1352.
- Moody, T. E., and J. Wright, 1995, *Adsorption Isotherms: North Carolina Apatite Induced Precipitation of Lead, Zinc, Manganese and Cadmium from Bunker Hill 4000 Soil*, BHI-00197, Bechtel Hanford, Inc., Richland, WA.
- Nimmo, J. R., D. A. Stonestrom, and K. C. Akstin, 1994, "The Feasibility of Recharge Rate Determination Using the Steady-State Centrifuge Method," *Soil Science Society of America Journal*, Vol. 58, pp. 49-56.
- Nriagu, J. O., 1974, "Lead Orthophosphates, Iv. Formation and Stability in the Environment," *Geochim. Cosmochim. Acta*, Vol. 38, pp. 887-898.
- Ruby, M. V., A. Davis, and A. Nicholson., 1994, "In Situ Formation of Lead Phosphates in Soils as a Method to Immobilize Lead," *Environmental Science and Technology*, Vol. 28, pp. 646-654.
- Skinner, H. C. W., 1987, "Bone: Mineral and Mineralization," in J. A. Albright and R. Brand (eds.), *The Scientific Basis of Orthopaedics*, Appleton and Lange, Norfolk, CT.
- Skinner, H. C. W., 1989, "Low Temperature Carbonate Phosphate Materials or the Carbonate-Apatite Problem," in Rex Crick (ed.), *Origin, Evolution and ModeM Aspects of Biomineralization in Plants and Animals, Proceedings of the 5th International Symposium on Biomineralization*, Arlington, TX, Plenum Press, NY.
- Skinner, H. C. W. and C. W. Burnharn, 1968, *Hydroxyapatite, Annual Report of the Director, Geophysical Laboratory*, Carnegie Institute, Washington, D. C.
- Stanforth, R. and A. Chowdhury, 1994, "In Situ Stabilization of Lead-Contaminated Soil," *Federal Environmental Restoration III and Waste Minimization II Conference Proceedings*, New Orleans.
- Stumm, W. And J. J. Morgan, 1981, *Aquatic Chemistry*, John Wiley and Sons, New York, NY.
- Wright, J. V., 1990a, "Conodont Apatite: Structure and Geochemistry," in Joseph Carter (ed.), *Metazoan Biomineralization: Patterns, Processes and Evolutionary Trends, 28th International Geological Congress, Paleontological Society and American Geophysical Union*, Washington, D.C., pp. 445-459.
- Wright, J. V., 1990b, "Conodont Geochemistry, a Key to the Paleozoic," in Willi Ziegler (ed.), *1st International Senckenberg Conference and 5th European Conodont Symposium (ECOS V) Contributions III*, Courier Forschungsinstitut Senckenberg, Frankfurt, Germany, pp. 277-305.

- Wright, J. V., J. F. Miller, and W. T. Holser, 1987a, "Chemostratigraphy of Conodonts Across the Cambrian-Ordovician Boundary: Western United States and Southeast China," in Ronald L. Austin (ed.), *Conodonts: Investigative Techniques and Applications*, Ellis Horwood, Ltd., London, pp. 259-286.
- Wright, J. V., H. Schrader, and W. T. Holser, 1987b, "Paleoredox Variations in Ancient Oceans Recorded by Rare Earth Elements in Fossil Apatite," *Geoch. Cosmoch. Acta*, Vol. 51, pp. 631-644.
- Wright, J. V., J. L. Conca, J. Repetski, and J. Clark, 1990, "Geochemistry and Microstructure of Conodonts from Jilin Province, China," in *1st International Senckenberg Conference and European Conodont Symposium Contributions III*, Courier Forschungsinstitut Senckenberg, Frankfurt, Germany, Vol. 118, pp. 307-332.
- Wright, J. V., L. M. Peurrung, T. E. Moody, J. L. Conca, X. Chen, P. P. Didzerekis and E. Wyse, 1995, *In Situ Immobilization of Heavy Metals in Apatite Mineral Formulations*, Technical Report to the Strategic Environmental Research and Development Program, Department of Defense, Pacific Northwest Laboratory, Richland, WA.
- Xu, Y. and F. W. Schwartz, 1994, "Lead Immobilization by Hydroxyapatite in Aqueous Solutions," *J. Contaminant Hydrology*, Vol. 15, pp. 187-206.

DISTRIBUTION**ONSITE (50 Copies)**U.S. Department of Energy
Richland Operations Office

K. M. Thompson	H0-12
A. C. Tortoso (2)	H0-12
DOE/RL Public Reading Room	H2-53

ERC Team

G. C. Henckel	H4-80
G. J. Jacksha	H9-02
M. C. Kelly	H9-03
A. J. Knepp	H4-80
T. D. LeFrancois	H9-03
T. E. Moody (30)	H9-03
S. W. Petersen	H9-03
R. P. Schroeder	H4-80
M. H. Sturges	H9-03
L. C. Swanson	H9-11
Document and Information Services (4)	H0-09
Hanford Technical Library	P8-55

Northwest Environmental Services Testing and
Training

J. Conca	H2-52
----------	-------

BHI-00857
Rev. 0