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Treatability Study of Reactive Materials to Remediate Ground Water Contaminated with Radionuclides, Metals and Nitrates in a Four-Component Permeable Reactive Barrier

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ABSTRACT

The treatment of a shallow multicontaminant plume of ^{239,240}Pu, ^{241}Am, ^{90}Sr, nitrate and perchlorate in Mortandad Canyon, Los Alamos, NM, was investigated in the laboratory using a multiple permeable reactive barrier consisting of four sequential layers. These layers include a polyelectrolyte-impregnated porous gravel for flocculating colloids, an Apatite II layer for plutonium, americium, and strontium immobilization, a layer of pecan shells as a biobarrier to nitrate and perchlorate, and a limestone gravel layer for any anionic species that may slip through the other layers, especially those of americium-carbonate. These layers can perform multiple functions, e.g., the pecan shells also sorb strontium very well and the Apatite II also remediates nitrate and perchlorate very well. Nitrate, perchlorate, plutonium, americium, and ^{90}Sr concentrations were reduced to below their maximum concentration limits (MCL) and usually to below detection limits in laboratory studies. The materials for this particular multiple barrier are inexpensive and readily available.

I. INTRODUCTION

The purpose of this study was to investigate the performance of alternative reactive barrier materials for possible use in a multiple permeable reactive barrier (PRB) at Mortandad Canyon. A barrier refers to anything that functions to prevent, bar, or retard the passage or movement of anything else, e.g., water, chemicals, trade goods, or ideas. In hydrology, traditional hydraulic barriers include impermeable walls, liners or caps made of bentonite, grout, asphalt, other clay minerals, precipitates of calcium carbonate or other chemicals, geotextiles, gels, or any material that can be made relatively impermeable. Containment of contaminant plumes can be accomplished by preventing the flow of the entire system, fluid and contaminant, through these conventional hydraulic barriers. Recently, more selective barriers have been developed that are barriers to one or a few components of the system, but not a barrier to the bulk of the system. Under unsaturated conditions, a capillary barrier consisting of a sharp boundary between two materials with greatly dissimilar pore sizes will act as an advective barrier to water but will not be a barrier to vapor flow. Likewise a saturated, compacted bentonite clay liner will act as an advective barrier to water and vapor but will not be a barrier at all to aqueous diffusion of molecular species for which sorption to bentonite is not significant, e.g., most anionic species. Permeable reactive barriers to particular chemical contaminants consist of a water permeable material with specific chemical reactivities towards one or more chemical constituents via mechanisms such as adsorption, exchange, oxidation-reduction, or precipitation. These barriers can have varying ranges of specificity, e.g., adsorption of specific species by a modified zeolite (Sullivan *et al.*, 1994), precipitation of metals and radionuclides by apatite (Conca *et al.*, 2000; Bostick *et al.*, 1999), or overall reduction of the system by zero valent iron, other iron phases, or microbial activity (Blowes *et al.*, 1997; Tratnyek *et al.*; 1997; Puls *et al.*, 1999).

PRBs can be emplaced physically by trenching and replacing the natural substrate with reactive media to form a wall of new material, or can be emplaced by mixing or injecting reactive components into the substrate. Either way, the migrating contaminant plume encounters the reactive material in the barrier, the contaminant is sequestered, altered or degraded and the water moves on through the barrier and exits the system successfully treated. PRBs require precise knowledge of both the hydraulic and chemical nature of the system. Impermeable barriers and PRBs can be used in combination to control both the hydrological and chemical nature of the treatment zone. Funnel and gate systems, or other systems that use impermeable barriers to channel ground water flow, are well suited for these applications (Starr and Cherry, 1994).

Mixed waste plumes will often require PRBs consisting of multiple layers of components configured specifically for a particular site and contaminants. Materials used in the field must be effective, inexpensive and readily available in multiple-ton quantities to be able to treat large volumes of water, or soil. Possible materials include zero valent iron, compost, apatites, MgO, carbonates, pecan shells, peat moss, lime, and other materials that have been investigated by researchers to varying degrees. In order to be cost-effective and produced in multiple ton quantities, most materials will come from mining production, agricultural waste production, or industrial waste production, with few modifying steps. The materials used in this study fit these criteria.

Radionuclides, including ^{90}Sr, ^{238,239,240}Pu, and ^{241}Am, have been detected since 1963 (LANL, 1997) in the shallow alluvial ground water system that exists in Mortandad Canyon at Los Alamos National Laboratory (LANL) in Los Alamos, New Mexico. These radionuclides are stable as dissolved species in the ground water and in the suspended phase where they adsorb onto colloids consisting of calcium carbonate, silica, ferric hydroxide, and solid organic carbon (LANL, 1997). Nitrogen species (nitrate and total Kjeldahl nitrogen) also occur in the alluvial ground water in Mortandad Canyon. Perchlorates have been discharged at concentrations above 1 mg/L (ppm) and occur in the Mortandad Canyon alluvial ground water at levels above 300 μg/L (ppb). Perchlorates were not monitored until recently because there were no regulatory limits. However, since the State of California recently instituted regulatory limits of 18 μg/L, and the United States Environmental Protection Agency (EPA) is considering an MCL of 32 μg/L for perchlorate, the concentrations in Mortandad Canyon may become a concern.

As a group, the contaminants in Mortandad Canyon can occur at concentrations up to several times the public dose limit (DCG) for the radionuclides or MCL for the nitrate and perhaps the perchlorate. Discharges into the canyon containing radionuclides, perchlorate, and nitrate have varied dramatically since 1963, generally dropping off with time. Most contaminants are assumed to come from the TA-50 water treatment facility near the head of the canyon, which presently discharges approximately 20,000 gallons per day over a short time period. Table 1 gives both discharge water chemistry from TA-50 during 1997 and some alluvial ground water chemistry at one of the Mortandad Canyon observation wells (MCO-3) in 1997 (LANL, 1997) just upstream of the proposed emplacement site of a multiple PRB. The chemistry of discharges and ground water vary greatly over time, e.g., nitrate varies from a few mg/L to over 50 mg/L.

The stratigraphy of Mortandad Canyon at the proposed PRB site consists of about 7 feet of alluvium composed of sand and gravel in a matrix of silt and clay overlying about 10 to 12 feet of clay and silt sediments that have resulted from weathering of tuff in place. A multiple PRB is proposed to be emplaced across the canyon near this point and down to the tuff bedrock to ensure maximum contact with ground water. The hydraulic conductivity of the sediments ranges from less than 10^{-5} cm/s locally in the silts and clays to 10^{-2} cm/s in the sands. Therefore, to avoid hydrologic complications in the overall flow in the canyon, the barrier materials need to be chosen with conductivities well above 0.1 cm/s to prevent plugging of the PRB. As will be discussed below, the materials chosen are gravel size and have conductivities greater than 1 cm/s, total porosities greater than 40%, and average pore sizes greater than 0.5 cm. Therefore, flux of ground water through the barrier will be determined by the hydraulic conductivity of the undisturbed sediments on either side of the barrier, plus any boundary properties that develop as a result of the barrier.

Numerous studies have been performed for zero valent iron, iron in other forms, polysulfides, granulated activated charcoal (GAC), and compost (Benner *et al.*, 1999; Blowes *et al.*, 1997; Fruchter, 1996; Tratnyek *et al.*; 1997; Puls *et al.*, 1999; Williamson *et al.*, 2000). Results of these studies are well known, having resulted in many field deployments (Goldstein *et al.*, 2000; Naftz *et al.*, 2000; Hocking *et al.*, 2000; Wickramanayake *et al.*, 2000). Sequential treatment has been investigated by researchers, including Morkin *et al.* (2000), who delineated the challenges facing treatment of multiple contaminants with multiple materials.

The multiple PRB chosen for this study and this site consists of four sequential layers: a polyelectrolyte-impregnated porous volcanic gravel for flocculating colloids, an Apatite II® layer for plutonium, americium, and strontium stabilization, a layer of pecan shells as a biobarrier substrate to nitrate and perchlorate, and a limestone gravel layer for anionic species that may not be trapped by the other layers, especially those of americium-carbonate. These layers can perform multiple functions, e.g., the pecan shells also sorb strontium very well and the Apatite II also remediates nitrate and perchlorate very well. The two types of gravels are inexpensive and easily available in ton quantities. The pecan shells are an agricultural waste that is easy to obtain in ton quantities and fairly durable in the subsurface given its high lignin content. The Apatite II is an inexpensive, primarily amorphous form of a carbonated hydroxy-apatite that has random nanocrystal of apatite embedded in it, resulting in efficient and rapid precipitation of various phosphate phases of metals and radionuclides. Apatite II is an efficient non-specific surface sorber and is readily available in multiple-ton quantities.

Table 1. Discharge water and alluvial ground water chemistry in Mortandad Canyon during 1997.

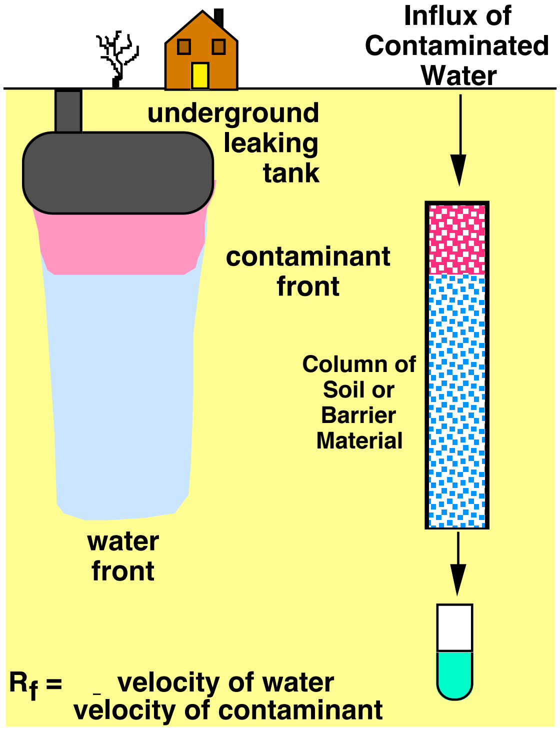
Constituent	Concentration in Discharge Water (mg/L or pCi/L)	DCG (pCi/L) or MCL (mg/L)	Concentration in Ground Water from well MCO-3 (mg/L or pCi/L)
Perchlorate	>> 1 mg/L	0.032 mg/L[a]	0.36 mg/L
^{238}Pu	11.39 pCi/L	1.6 pCi/L	16.2 pCi/L (4.0x10^{-15} *M*)
^{239,240}Pu	4.58 pCi/L	1.2 pCi/L	12.5 pCi/L (8.4x10^{-13} *M*)
^{241}Am	58.0 pCi/L	1.2 pCi/L	14.1 pCi/L (1.7x10^{-14} *M*)
^{90}Sr	28.5 pCi/L	8.0 pCi/L	20.2 pCi/L (1.6x10^{-15} *M*)
Nitrate	68 mg/L	10 mg/L	3.86 mg/L
Ammonium	2.15		--
Calcium	102		22.1
Magnesium	0.5		2.8
Potassium	11.7		7.9
Sodium	140		40
Silica	50.7		46
Iron	<0.01		--
Bicarbonate	251		105
Carbonate	24.4		--
Sulfate	28		12.0
Chloride	24.4		8.0
Fluoride	1.01		1.08
Total Dissolved Solids	686		274
pH	8.47		7.5
specific conductance (μS/cm)	1,372		288
ionic strength	0.0137 *M*		--

[a] possible regulatory limit being proposed

II. MATERIALS AND METHODS

Past investigations and feasibility test results were used to focus on a design for the multiple PRB in Mortandad Canyon. Results are described in the following sections. Batch tests and one dimensional (1–D) column tests conducted using Mortandad Canyon ground waters and reactive media are also described below. On the basis of these results, large-scale columns and aquifer-box tests were conducted as the final feasibility tests prior to emplacement, and the results were used for the final emplacement design. Figure 1 gives a schematic of how batch and column tests were used to reflect field conditions. Analytical techniques included Ion Chromatography, Inductively Couple Plasma (ICP) Emission and Mass Spectroscopy, Liquid Scintillation Counting, Transmission Electron Microscopy plus standard methods for measuring pH and dissolved oxygen.

Ground water collected directly from Mortandad Canyon was used as the stock solution in all new feasibility studies (LANL, 1997). For contaminated studies, plutonium, americium, strontium, nitrate, or perchlorate were added in sufficient quantities for particular experiments. A large volume of uncontaminated ground water was collected from Mortandad Canyon well MCO-5 for subsequent laboratory studies.



$$R_f = \overbrace{V_w/V_c}^{\text{from column tests}} = \overbrace{1 + K_d(\rho_b/\theta)}^{\text{from batch tests}}$$

R_f = the retardation factor
θ = volumetric water content
(= porosity if saturated)
ρ_b = the bulk density
K_d = the distribution coefficient
(amount on solid ÷ amount in solution)
V_w = the velocity of the groundwater front
V_c = the velocity of the contaminant front

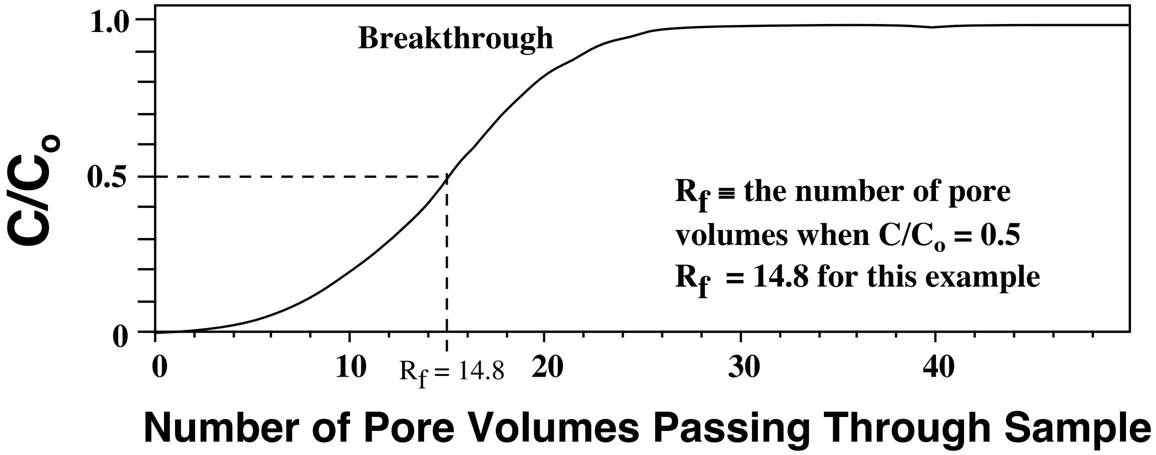


Figure 1. Definition of the Retardation Factor and contaminant breakthrough behavior. Batch and column studies are related to behavior in the field by the above relationship. The S–shape of the breakthrough curve reflects hydrodynamic dispersion. The number of inflection points, the shape of the curve and the absolute position along the axis reflect the number, distribution and type of sorption sites. C/C_o is the concentration of the specific chemical species in the effluent solution divided by the concentration in the starting solution.

Batch sorption studies were performed as initial screening tools for evaluating solid media. Batch studies generally consisted of a small amount of substrate combined with 10 times the amount of contaminated water by mass. The combination is shaken for 24 hours or longer depending upon the estimate of kinetic reaction times. The concentration of contaminant in the water was measured to determine how much contaminant had been removed from solution by interaction with the substrate.

Column studies were performed to reflect more relevant field conditions. These studies monitor the contaminant concentrations and other solution properties in the effluent exiting the column following contact with reactive media. Results are often given as a breakthrough curve that shows the normalized concentration of the contaminant as a function of the number of pore volumes exiting the column (Figure 1). This normalizes the tests to any size system. The 1-D column studies were small-scale columns 4.8 cm in inside diameter and 6 to 10 cm in length. These were loaded with small grain-size splits of the various materials and run at a range of flow rates to provide a scientific basis and design criteria for larger columns. Flow rates were up to five times the natural velocity of ground water in Mortandad Canyon. Data from these types of column studies were also used to evaluate rate-limited immobilization of contaminants. Feasibility studies with larger columns, in which flow rates, material sizes, and juxtaposition of materials were scaled closer to actual field conditions, were performed as a test of the multiple PRB. In addition, two-dimensional (2-D) aquifer cell studies were performed to approach a realistic remediation scenario with the media contacting each other *in situ*.

A. BARRIER MATERIALS

1. Porous Gravel

A porous gravel coated with a material to capture colloids was chosen as the first layer in the PRB to retard or prevent the movement of colloids in the Mortandad Canyon ground water. There is significant evidence indicating that enhanced transport of actinides occurs in subsurface geologic media through their association with colloid-sized particles in ground water, resulting in colloid-facilitated transport (Kersting, *et al.*, 1999). The colloids have a high potential for adsorbing these contaminants because of their large surface area and generally negative charge. The resulting pseudo-colloids, i.e., contaminants attached to the surface of silica, clay, iron oxides and other non-contaminant colloidal materials, move greater distances faster than dissolved species in subsurface aquifers. These colloid-sized contaminants include radionuclides, metals, pesticides, organics, viruses, and bacteria, and synthetic materials such as asbestos fibers. The transport of radionuclides as pseudo-colloids has been described recently by many authors at multiple DOE sites, including LANL, the Nevada Test Site and others (Triay *et al.*, 1997). The rapid movement of colloidal contaminants through the subsurface is also the subject of numerous modeling studies as cited by Kale (1993).

Kale (1993) developed a concept of a colloid barrier using glass beads and a cationic, highly soluble polyelectrolyte with the ability to capture and agglomerate colloids. The polyelectrolyte used was a commercially available material, polydialylldimethylammonium chloride, named Catfloc®. This material is used in the wastewater treatment industry to flocculate small particles, and was selected for its ability to adsorb onto silica substrates, e.g., silica colloids, rock, or glass beads. Catfloc also was chosen for this study because of the low concentrations necessary for good performance, the relatively low cost, and because it is not easily biodegraded. The laboratory-scale studies used glass beads and cm-sized rock chips of the gravel layer and Mortandad Canyon ground water with and without colloids, at concentrations of 2 x 10^8 particles/mL. The biodegradability of Catfloc was evaluated in studies where Catfloc acted as the sole carbon source in a nutrient culture medium inoculated with Mortandad Canyon ground water. The culture medium also contained potassium nitrate and sodium phosphate as a supply of nitrogen and phosphorous nutrients to ensure that nutrient deficiency was not a growth-limiting factor. Aliquots of the culture medium were taken and stained for total microbial counts.

2. Apatite II

A special form of the mineral apatite, Apatite II, was chosen as the second layer in the PRB to treat metals, particularly Pu. Feasibility studies were performed to determine the metal-stabilization potential of various materials with respect to acid mine drainage in northern Idaho and actinide-contaminated waters at DOE sites (Wright *et al.*, 1995; Conca, 1997; Bostick *et al.*, 1999; Conca *et al.*, 2000; Runde, 2000). Materials investigated included different sources of apatite (various mineral sources, synthetic, commercial, cowbone charred or uncharred, and Apatite II), zeolites (clinoptilolite and chabazite), various polymers including Dowex II, C-sorb, Cabsorb, Mersorb, peat moss, zero valent iron, hematite, goethite, and activated charcoal. The Apatite II performed the best with respect to all metals studied, i.e., lead, cadmium, zinc, uranium, strontium, and plutonium, but with different mechanisms depending upon the metal and the conditions. Because of this generally good performance for many metals under various conditions, Apatite II was chosen for this Mortandad Canyon study.

The Apatite II can be obtained in almost any grain size from powdered to gravel size. The gravel size has hydraulic conductivities exceeding 10 cm/s and a bulk density between 0.5 and 1.0 g/cm^3. Apatite is ideal for stabilizing many metals because it instigates heterogeneous nucleation of metal-apatite phases under environmental conditions (Lower *et al.*, 1998). The excellent stabilization efficiency comes from the extremely low solubility products of the resultant metal-apatites, e.g., for uranium–phosphate (autunite) $K_{sp} = 10^{-49}$, and for lead–apatite (pyromorphite) $K_{sp} = 10^{-76}$. Table 2 lists some solubility products as examples (the reactions are given in MINTEQ-A2; Geochem Software Inc. 1994). There are several apatite sources with widely varying reactivities and properties, but most are not appropriate for metal remediation. For best results, the apatite should: 1) have as much carbonate ion substituted as possible, 2) have no fluorine substitution, 3) have no trace metals initially in the structure, 4) be poorly crystalline or even amorphous, and 5) have high internal porosity (Conca *et al.,* 2000). For these reasons, traditional phosphate ores and cow bone, charred or not, are not as effective as Apatite II.

Table 2. Stabilities of Some Relevant Phases (from MINTEQ-A2; Geochem Software Inc. 1994)

Mineral Phase	Solubility Product (log K_{sp})	Mineral Phase	Solubility Product (log K_{sp})
$Pb_5(PO_4)_3(OH,Cl)$	-76.5	$Am(PO_4)$	-24.8
$Ca(UO_2)_2(PO_4)_2 \bullet 10H_2O$	-49.0	$Pu(PO_4)$	-24.4
$Sr_5(PO_4)_3(OH)$	-51.3	UO_2HPO_4	-10.7
$Zn_3(PO_4)_2$	-35.3	$Cd_3(PO_4)_2$	-32.6

The nominal composition of Apatite II is $Ca_{5-x}Na_x(PO_4)_{3-x}(OH)(CO_3)_x$ where $x < 0.2$. The high reactivity of Apatite II relative to other apatites comes from the unusual structure of the solid. Most of the material is amorphous hydroxy calcium phosphate with respect to both XRD and to TEM. However, there are random nanocrystals of well-crystallized apatite embedded throughout the amorphous phase (Figure 2). Also, there is substantial carbonate substitution which makes the structure less stable and more reactive (Wright *et al.*, 1990). However, once metals are in the apatite structure, it is much more stable than the initial Apatite II. Because of this arrangement, the amorphous structure is relatively reactive and provides a sufficient excess of phosphate ion to solution, locally exceeding the solubility limit of many metal-phosphate phases and resulting in precipitation, particularly for lead, uranium and plutonium. At the same time, the nanocrystals provide the apatite structure for nucleating the precipitates. Other apatites, such as phosphate rock, bone char, or reagent grade tricalcium phosphate, are crystalline (Figures 3 and 4), have little or no carbonate substitution, have substantial fluorine substitution, have significant trace metal substitution (strontium, barium, uranium and others), or have less microporosity, all of which reduce the reactivity and make them less optimal for metal stabilization. The concentration of phosphate ion in solution in equilibrium with Apatite II is in the 10 to 100 µg/L (ppb) range, and depends upon solution chemistry, particularly pH. It is important, however, because these low values avoid the phosphate loading issues common to organophosphates and soluble inorganic phosphates such as most fertilizers.

Figure 2. HR-TEM image of Apatite II showing general amorphous nature with random nanocrystal inclusions of crystalline apatite (low–resolution image is inserted in upper left corner).

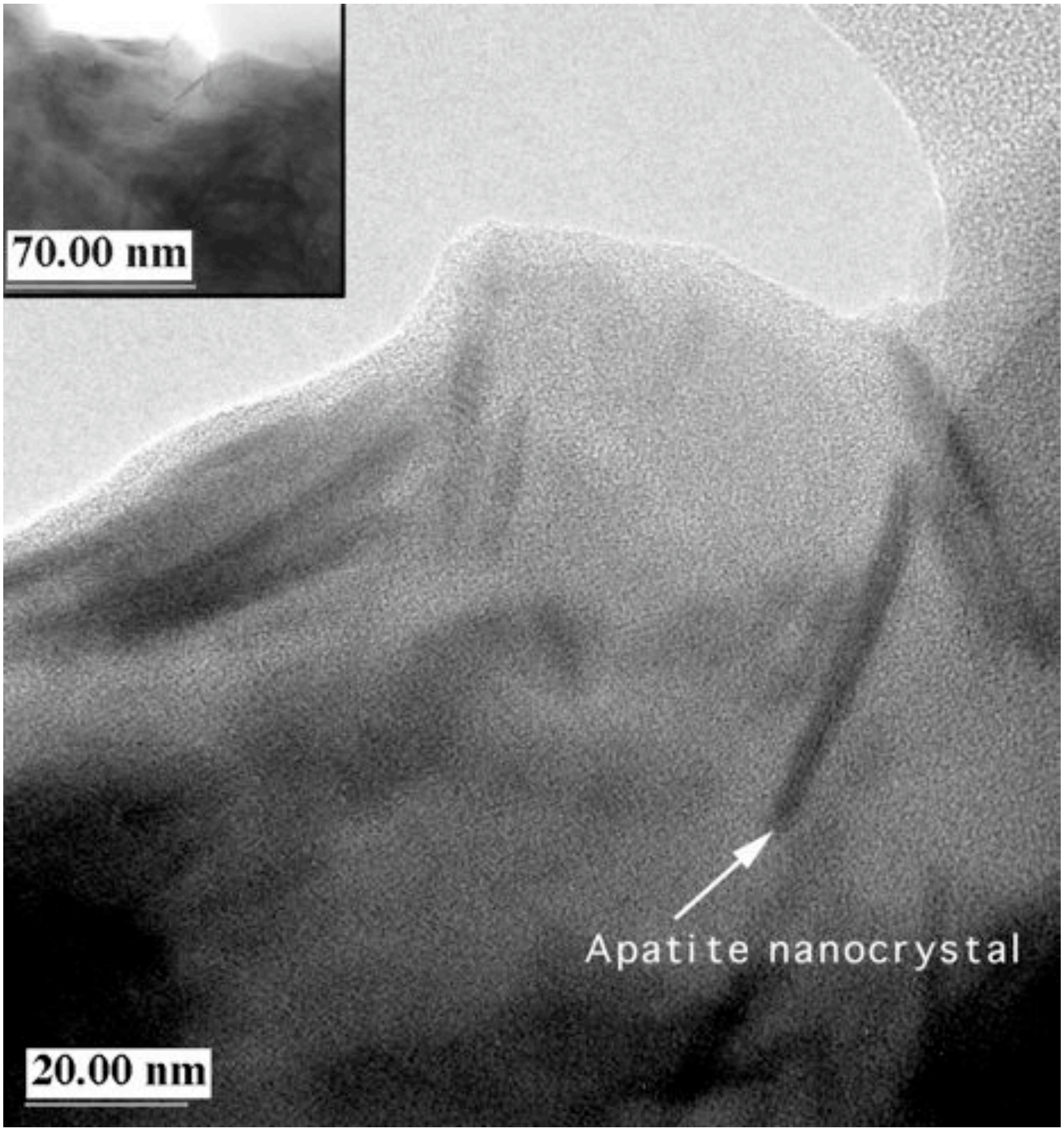


Figure 3. HR-TEM image of mineral apatite (NC phosphate rock) showing the crystalline nature of the apatite.

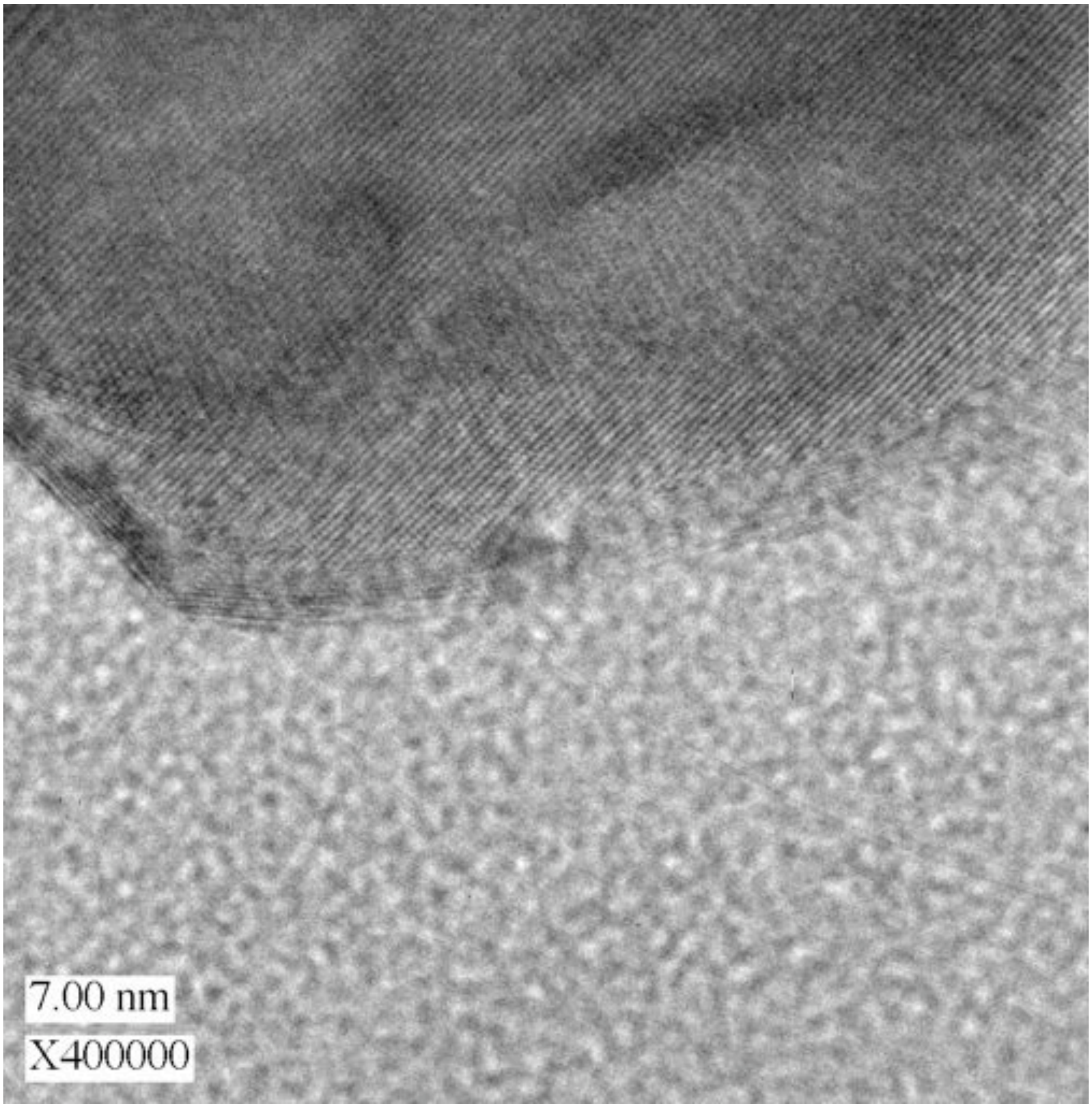
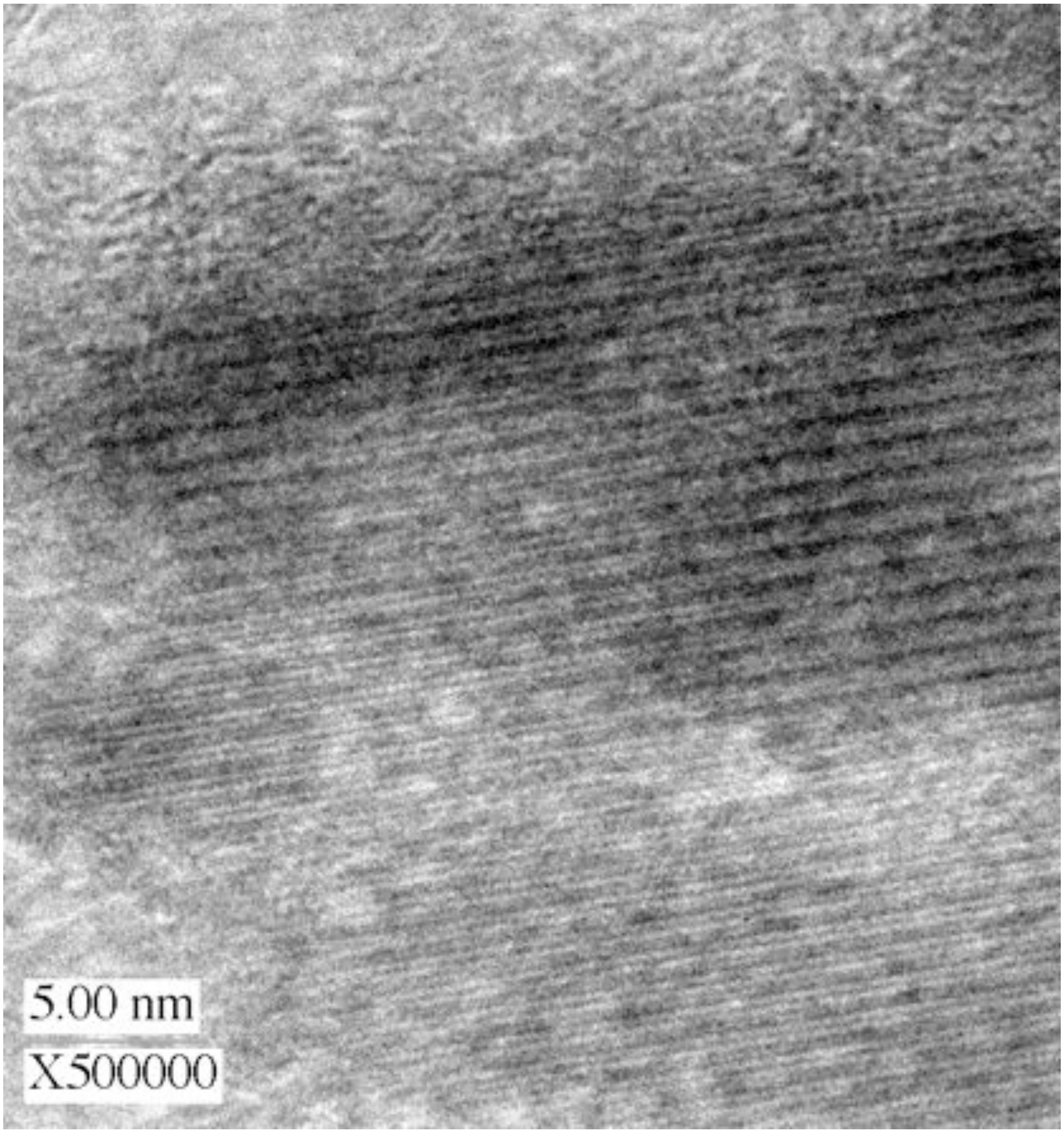


Figure 4. HR-TEM image of bone char showing the crystalline nature of the apatite.



The Apatite II was found to leach ^{87}Sr at a constant concentration, regardless of the strontium concentration in the influent water. For batch tests with radioactive ^{85}Sr, this was not a problem as the two isotopes are easily distinguished. However, during the column studies that could used only ^{87}Sr because of laboratory activity limits, there was no way to distinguish the difference between ^{87}Sr leached from, or sorbed onto, the Apatite II. It was found that ^{87}Sr leached from the Apatite II in columns at a constant concentration of 0.85 mg/L, regardless of influent concentration, e.g., columns with influent ^{87}Sr concentrations of 2 mg/L or 0 mg/L both showed effluent concentrations of about 0.85 mg/L. The column study described in Section III.B.3 used ^{85}Sr and so avoided this problem. Further studies will use only ^{85}Sr. It is not known whether the^{87}Sr leaching from the Apatite II was coming from the amorphous phosphate phase or from the organics.

3. Pecan Shells

Pecan shells were chosen as the third layer in the PRB to treat nitrate and perchlorate. In the case of nitrate, biodegradation has been widely investigated, and the microbial processes are well understood (Zumft, 1999). Nitrate can be removed from contaminated water by either assimilatory or dissimilatory processes. Assimilatory processes result in ammonia production and uptake, with subsequent conversion to cellular constituents such as protein and nucleic acids. Dissimilatory nitrate reduction processes result in gaseous products, such as nitrogen gas, nitric oxide and nitrous oxide. The microbial reduction of perchlorate has only recently been demonstrated (Attaway and Smith, 1993; Herman and Frankenberger, 1998; Wallace *et al.*, 1998), but field-scale studies for bioremediation of this contaminant have not been reported.

In a PRB system where one of the barriers is a biobarrier, the catalyst for the destruction of nitrate is the indigenous microbial population, which uses nitrate as both a nitrogen source, and as an electron acceptor under denitrifying conditions. The catalyst for perchlorate destruction is also microbial in nature, where the perchlorate is reduced to non-toxic chloride products, but less is known about the reduction pathways, and the physiological requirements and identities of the organisms involved. Frequently, the only missing element for destruction of both of these anionic species is carbon, which can be supplied by an appropriate material added to the biobarrier, e.g, residual organics on the Apatite II.

Pecan shells were the carbon-based support material chosen for the biobarrier section of the multiple PRB. It does not serve as an efficient carbon source but as an efficient substrate upon which to form biofilms. This agricultural waste product fits the needs of this system very well insofar as it is inexpensive, can be obtained in ton-quantities as gravel-sized particles with large average pore sizes, has great porosity and surface area for attachment of biofilms, persists in the subsurface because of its high lignin content, and has no disadvantageous reactions with the other barrier materials. This study has taken an empirical approach to development of this biobarrier. The ability of the biofilms that form on the pecan shells to reduce the nitrate present in ground water has been determined, as have the nitrogen-based reduction products that are present and in what amounts. The populations of bacteria have been determined using a Most Probable Number (MPN) technique that measures viable bacterial cells that will grow in nitrate-amended media under denitrifying conditions.

4. Limestone Gravel

Actinides form strong carbonate complexes in aqueous solutions, especially U and Am (Triay at al., 1991; Runde *et al.*, 1992). In Mortandad Canyon, Am appears to form carbonate complexes and may pass through the other layers (LANL, 1997). However, in many laboratory studies for the Yucca Mountain Project and for other nuclear waste programs, it has been observed that actinide carbonate complexes will sorb strongly to carbonate rocks (Triay *et al.*, 1991; Triay *et al.*, 1997). Therefore, the final layer in the PRB was chosen to be limestone gravel.

B. BATCH TEST METHODS

Batch sorption studies were performed on a set of aggregate materials to determine the reactive sorption coefficient (K_d) of radionuclides in MCO-5 water. Ten potentially reactive materials and mixtures of materials were analyzed in this study, as summarized in Table 3. Apatite refers to Apatite II except when designated mineral apatite. Various treatments of Apatite II were performed to observe any change in reactivity.

The aggregate materials were mainly used as received; no crushing or size separation was performed. However, the coagulant treated gravel was prepared by first cleaning the gravel in weak (~0.15 M) hydrochloric acid by overnight soaking. Next, the gravel was rinsed in MCO-5 water and immersed in a colloidal coagulant polymer solution (Catfloc ~2 g/L) overnight. Finally, the gravel was given a final rinse in MCO-5 water and kept immersed in MCO-5 water to guard against unknown effects of allowing the coagulant-treated gravel to dry.

Apatite II samples that were treated with phosphoric acid were prepared by overnight soaking in 0.5 *M* phosphoric acid followed by rinsing in MCO-5 water and air drying. As will be seen below, this treatment did not increase performance sufficiently to warrant its use in the field. Any field application will use the Apatite II as received in the specified grain size, and not treated in any way.

Three radionuclides were utilized in these batch tests: $^{85}Sr^{2+}$, $^{239}Pu^{5+}$ and $^{241}Am^{3+}$. ^{85}Sr concentrations were quantified using a Packard Cobra Gamma Counter, whereas both ^{239}Pu and ^{241}Am were analyzed on a Packard Model 2500 liquid scintillation counter (LSC). Separate batch sorption studies were repeated for each radionuclide. The ^{85}Sr batch sorption study used a liquid to solid ratio of approximately 10:1 (150 mL solution and 15 g solid). The studies with ^{239}Pu and ^{241}Am used a liquid to solid ratio of approximately 15:1 (225 mL solution and 15 g solid). Apatite/limestone mixtures were formed by adding 2 additional grams of limestone, an amount that only slightly modified the liquid-solid ratios. The starting concentration of each radionuclide solution was 7.6×10^{-9} *M* ^{85}Sr, 2.4×10^{-8} *M* ^{239}Pu, and 8.5×10^{-12} *M* ^{241}Am.

Table 3. Summary of Reactive Materials and their Properties.

Material	Acronym	Size distribution	Source
Gravel	GRAV	1 – 3 cm	Los Alamos Transit
Coagulate treated gravel	CGRAV	1 – 3 cm	Los Alamos Transit
Mineral apatite	AP	0.1 – 0.5 cm	PCS, Inc.
Apatite II	UF	0.5 – 3 cm	UFA Ventures
Apatite II treated with phosphoric acid	FWP	0.5 – 3 cm	UFA Ventures
Apatite II mixed with limestone	UFWL	0.5 – 3 cm	UFA Ventures & La Farge Mining
Apatite II treated with phosphoric acid and mixed with limestone	FWPL	0.5 – 3 cm	UFA Ventures & La Farge Mining
Limestone	LIM	1 –2 cm	La Farge Mining
Clinoptilolite	ZEO	0.5 – 1 cm	St. Cloud Mining
Pecan Shells	PS	1 – 2 cm	San Saba Pecans

Aggregate materials were equilibrated with water from well MCO-5 before batch sorption procedures began. Dry aggregates were weighed out and placed in 250 mL round Teflon® bottles with sterilized water from well MCO-5 and agitated for 2 weeks prior to beginning batch studies. Agitation was accomplished by placing the bottles horizontally onto laboratory shakers. At the completion of the 2-week equilibration phase, the solids were drained of water from well MCO-5, water from well MCO-5 containing a spike of known radionuclide concentration was added, and agitation continued.

Water from well MCO-5 was sampled and analyzed over time to determine sorption behavior and kinetics. Sampling of the container solutions was performed using pipettes. To remove particulates, each sample was centrifuged at 16,500 rotations per minute for an hour in Teflon vials. Samples were then split for radionuclide and water chemistry analysis. Since the ratio of liquid to solid changed for each sample interval, solution volumes were carefully measured and accounted for in calculating the sorption coefficient isotherms.

For the biobarrier studies, pecan shells (2 g), or pecan shells and dog food (2 g/0.2 g) were loaded into Oak Ridge tubes and 20 mL of water from well MCO-5 was added for a solution/solid ratio of 10:1 (and a pecan shell/dog food ratio of 10:1). Reaction tubes were incubated at room temperature on a shaker. Successive samples were taken on the day after the tubes were loaded, Day 1, and on Day 2, Day 7, Day 14, and Day 21 in most cases. Nitrate, nitrite, and ammonia concentrations were determined using EPA method 300.0, an ion chromatographic method. MPN analysis involved the use of a nitrate-reducing MPN method developed from methods found in Microbiological Methods 7th edition (Collins *et al.* 1995).

C. COLUMN TEST METHODS

1. Single Column Tests with ^{87}Sr, Nitrate, and Colloids

A single column study to evaluate pecan shells with respect to nitrate, strontium and colloids in water from well MCO-5 used single 6-cm long, 4.8-cm inside diameter columns. The column was packed with pecan shells with no food source, and was infused with water at a flow rate of 0.13 mL/min. The ground water was spiked with 2 mg/L ^{87}Sr, 50 mg/L $NaNO_3$ (for a total nitrate concentration of 100 mg/L) and 2x10^8 fluorescent colloids per L of water. Fluorescent polymer (polystyrene) microsphere colloids (1μm) were obtained from Duke Scientific Corp., Palo Alto, CA. Sieve analysis of the pecan shells indicated that 75.9% of the shells were 2.00-4.75 mm in size while 24.1% were 1.00-2.00 mm in size. Approximately 6.5-mL aliquots were retrieved automatically by an Isco® Foxy Junior fraction collector. ICP analysis of ^{87}Sr and nitrate-ion chromatography were performed on the effluent following collection from the column, while the fluorescent colloids were counted using a microscopic technique (Abdel-Fattah and Reimus, 2000).

2. Sequential Column Tests with ^{87}Sr and Nitrate

Four 1–D columns were arranged in sequence to evaluate the ability of various reactive media to remove contaminants from flowing ground water. These columns were packed with materials selected based on the results of the batch sorption treatability studies, and run at a range of flow rates up to 5 times the natural velocity of ground water in Mortandad Canyon. Material included gravel coated with Catfloc, volcanic rock (basalt) coated with Catfloc, Apatite II, pecan shells, pecan shells mixed with dog food (10:1, respectively), and limestone.

MCO-5 water was spiked with various contaminants to desired concentrations. Columns were packed with various reactive media through which contaminated ground water was flushed at a constant flowrate. The columns were constructed of borosilicate glass with a 4.8 cm inside diameter and are equipped with an adjustable endplate for bedlength variation from 1-13 cm.

All media used in the four sequential columns were sieved to less than 4.75 mm size fraction but greater than 1.00 mm. Catfloc-coated gravel or basalt was prepared by contacting 2 g/L Catfloc solution with the gravel or basalt overnight on a rotator (60 rpm; approximately 2:1, liquid-solid ratio). Apatite II was used as obtained or was soaked in 90^{o}C hot water to further remove residual organics. Pecan shells were used as received or crushed to the desired size fractions. In the first column study only, dog food was added to the pecan shells (1:10, dog food:pecan shells) to serve as a carbon source stimulant for microbial growth. All column studies were designed to run until breakthrough, however, the Los Alamos Cerro Grande fire resulted in complete shut down of the study before breakthrough was achieved.

3. Sequential Large-Scale Column Tests with ^{239}Pu, ^{241}Am, ^{85}Sr, Nitrate, and Perchlorate

Four columns were manufactured and machined from transparent acrylic sheets and tubing. The columns measured 5.5 inches (~14 cm) in internal diameter and 12 inches (~30 cm) in length. Two insteps were milled into each end of the acrylic tubing to allow the emplacement of perforated Teflon rings. The perforated rings created an area of dead volume and slight backpressure to allow dispersion of the tracer before contacting the column media. Flow ports were established on each endcap of the columns using 1/4 X 28 thread peek flow fittings.

Four aggregates were chosen for use in the columns. The selection of materials was based on the batch sorption studies. The columns were packed with these materials and filled with MCO-5 water. The columns were filled with de-aerated water and purged of large air pockets. No attempts were made to eliminate small air bubbles. The columns were connected inline to each other via 1/16 inch ID Teflon tubing. De-aired MCO-5 water was pumped through the columns so that flow introduced into the first column flowed through the second, third, and out the fourth, respectively. Column media was equilibrated with MCO-5 water by flushing the water through the columns at approximately 20 mL/hr for two weeks prior to injection of contaminants. Prior to injecting the column network with spiked MCO-5 water, the columns were equilibrated to the injection flow rate by adjusting the pump's flow rate to the planned injection rate 72 hours in advance of the injection. The pore volume of the column network was slightly greater then 11 liters, distributed approximately equally within the 4 columns.

A 100 mL pulse of MCO-5 water spiked with 7×10^{-9} *M* ^{85}Sr, 5×10^{-7} *M* ^{239}Pu (750,000 pCi) and 1×10^{-9} *M* ^{241}Am was injected into the columns after the two-week equilibration period. This plutonium concentration represents about 600,000 times the field concentrations, about 60,000 liters at the field concentrations, or about 60 years of flow at present plutonium concentrations. This strontium concentration represents about 440,000 times the field concentrations, about 44,000 liters at the field concentrations, or about 44 years of flow at present ^{90}Sr concentrations. This americium concentration represents about 100,000 times the field concentrations, about 10,000 liters at the field concentrations, or about 10 years of flow at present ^{241}Am concentrations. Nitrate and perchlorate were at the field concentrations of 3.9 mg/L and 0.4 mg/L, respectively. No colloids were injected as part of this particular column study. The purpose of the pulse was to see if rapid contaminant loading would be stable against future flow, or if sorbed radionuclides would be remobilized. The spiked water was injected via a KD Scientific® syringe pump. After a one-hour injection, a Scilog Chemtec® piston pump then maintained the approximate 100 mL/hr flow of uncontaminated MCO-5 water. Initially, an Isco Foxy® funnel fraction collector was used to collect the elutants hourly into Teflon collection bottles. After the first 3 days, this was changed to a large collection bottle sampled approximately every 72 hours. The elutants were analyzed for radionuclide breakthrough and solution chemistry. Radionuclide breakthrough was analyzed using the same instruments as described in the batch sorption studies. However, because the plutonium and americium have similar radioactive energy emissions, differentiating between these two radionuclides was not done. Only an analysis of gross alpha decay was performed. Direct analysis of ^{85}Sr was possible because ^{85}Sr is the only gamma emitter in the study.

4. 2-D Aquifer Box Tests with ^{87}Sr, Nitrate, and Perchlorate

A 2-D aquifer cell was manufactured from aluminum. The inside dimensions of the rectangular box were 32 cm (height) x 62 cm (length) x 5 cm (width). Rectangular end chambers, constructed of aluminum alloy, were screened over the entire vertical height of the box. The bottom and back of the box were aluminum and a glass plate served as the front (see Figure 12 in Section III.B.4). The pore volume of the cell was approximately 2 L. ^{87}Sr and perchlorate in water from well MCO-5 were at concentrations of 2 mg/L and 300 μg/L, respectively. During the first 60 days, the influent nitrate concentrations were held constant at approximately 125 mg/L. Thereafter, the nitrate concentrations were increased to 250 mg/L in order to evaluate the ability of microorganisms in the PRB materials to reduce irregular nitrate concentrations. The cell was constructed to allow discrete sampling between each layer interface.

III. RESULTS

A. BATCH TESTS

1. Colloid Tests in Mortandad Canyon Ground Water

The laboratory-scale studies used glass beads and cm-sized rock chips of the gravel layer and Mortandad Canyon ground water with and without colloids at concentrations of 2×10^8 particles/mL. These studies were performed to determine the effect of a number of different parameters on agglomeration of microspheres on the cm-sized rock surfaces. There was a strong dependence on Catfloc concentration and colloid concentration, but the presence of Catfloc generally increased colloid removal from solution by at least three orders of magnitude. The Catfloc was not significantly degraded after 1 year.

2. Batch Tests for ^{239}Pu, ^{241}Am, and ^{90}Sr in Mortandad Canyon Ground Water

Results of the batch sorption studies are presented as K_d versus time for ^{239}Pu, ^{241}Am, and ^{85}Sr in Figures 5, 6, and 7, respectively. The results indicate that untreated Apatite II has a large affinity for all three radionuclides. All combinations of Apatite II displayed large affinities for plutonium. Limestone/untreated apatite mixtures and treated Apatite II also display large affinities for americium. Apatite II has greater affinities for all three radionuclides compared to mineral apatite.

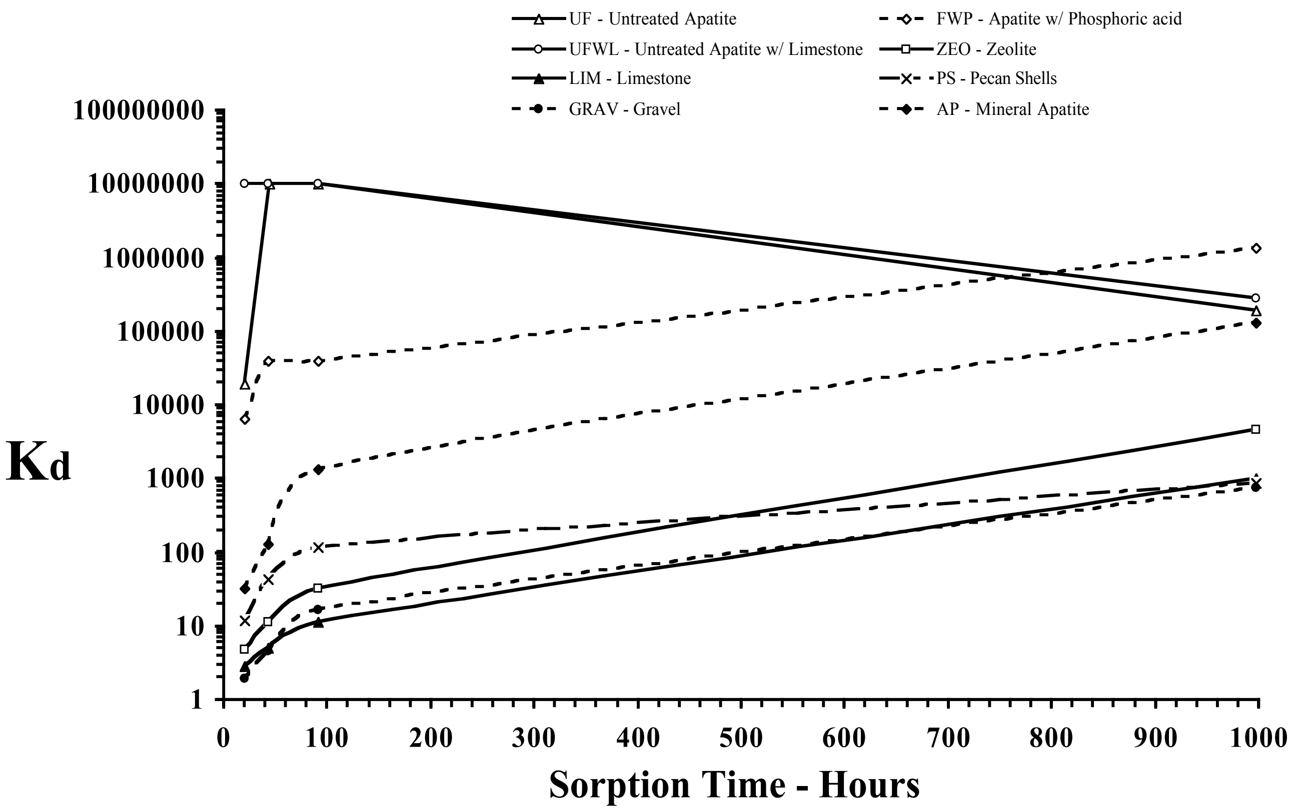


Figure 5. Sorption of Pu-239 Over a 42-Day Time Span

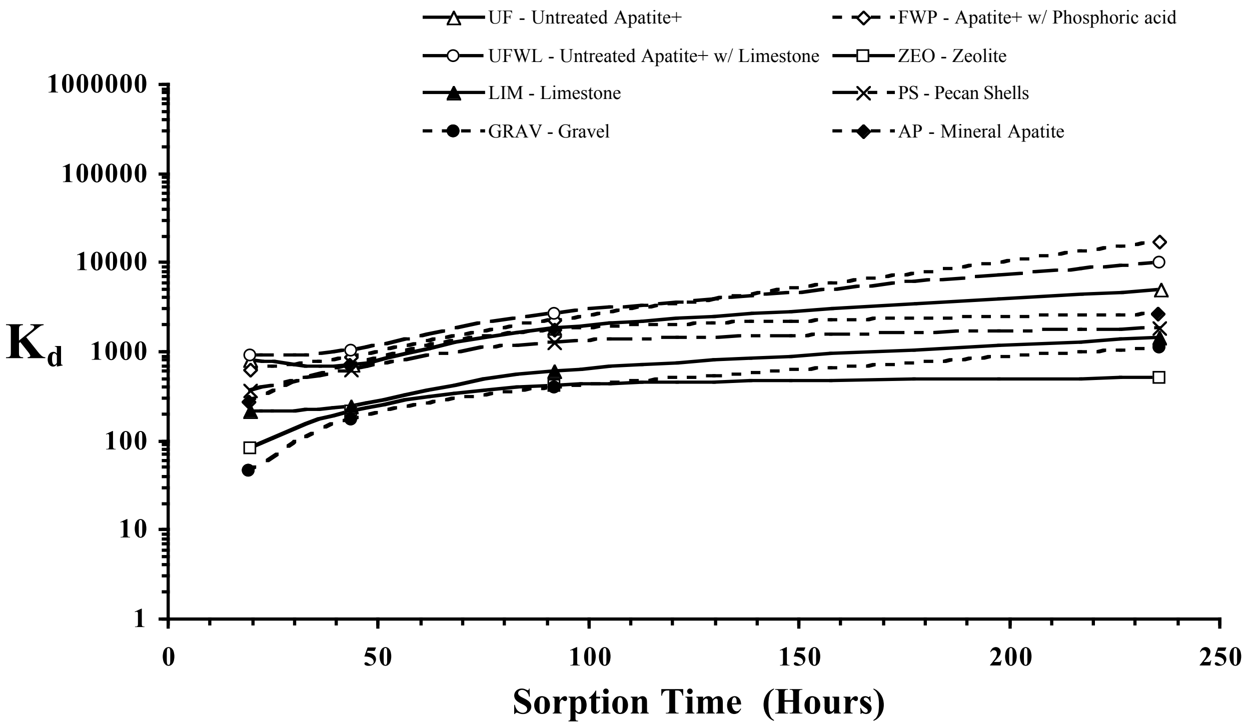


Figure 6. Sorption of Am-241 Over a Ten-Day Time Span

Materials that will function as components of the multiple PRB, such as pecan shells in the biobarrier, were evaluated in batch sorption studies to determine radionuclide capture properties. These materials displayed much less affinity for radionuclides than apatite.

Although the amounts of plutonium used were too small for phase identification, the extremely high K_d values are consistent with the extremely low solubilities of plutonium-phosphates and consistent with studies of apatites showing precipitation with respect to lead and uranium (Ma *et al.,* 1993; Moody and Wright, 1995; Bostick *et al.,* 1999; Runde, 2000). For plutonium, the various samples of apatite exhibited the highest sorption values. The mineral apatite was slower to react than the Apatite II, but eventually reached the same levels. The other materials still showed reasonably high K_d values for plutonium, up to 1,000. For americium, the apatites exhibited K_d values between 1,000 and 10,000, and the other materials had K_d values below 1,000. ^{85}Sr showed the least sorption affinity for any of these materials. While Apatite II performed the best with K_d values of about 500, all were less than 1,000. The large amount of ^{87}Sr that leached from the Apatite II during column tests makes it difficult to evaluate these batch tests with ^{85}Sr. There was probably significant isotopic exchange which may account for most of the sorption. Geochemically, strontium has a strong affinity for apatite phases and readily precipitates in phosphate phases in nature, including co-precipitation with calcium in bone materials (Wright, 1990). The poor showing in laboratory tests may also reflect kinetic effects.

3. Biobarrier Batch Tests for Nitrate

The biobarrier support material selected was pecan shells. Batch tests were performed to determine the effects of initial sterilization of materials, effects of readily available food sources, the efficiency of the medium, and the time necessary for inducing microbial population growth to sufficient levels to reduce nitrate concentrations in the groundwater. The effect of a food source on the microbial activity was investigated using dry dog food as a readily accessible food source. Two studies were used to determine the amount of bacterial growth and contaminant degradation in nitrate (NO_3)-contaminated water. Each study contained 5 different sets of samples: 1) the water and the pecan shells were both sterilized (sterile control), 2) the pecan shells were sterilized, the water was non-sterile thereby providing the bacteria (sterile PS, unsterile H_2O), 3) the water was sterilized, the pecan shells were not (unsterile PS, sterile H_2O), 4) both the water and the pecan shells were non-sterile (unsterile control), and 5) filtered nitrate-contaminated water without any substrate. Duplicate samples were run under each set of conditions in each study. Another set of experiments were run with dog food as an additive along with pecan shells. Experiments were run both with field concentrations of nitrate (~20 mg/L) and with high nitrate (~600 mg/L).

Results for the pecan shells alone with the 600 mg/L nitrate-contaminated groundwater are shown in Figure 8. These results are similar for all runs. All filtered water samples with no substrate showed no reduction in nitrate concentrations. Sterilizing the substrates (pecan shells or the pecan shells and the dog food) diminished the degree of nitrate reduction more than sterilizing the groundwater. Experiments with non-sterilized media resulted in greater reduction of nitrate and shorter induction periods needed to form a sufficiently active microbial population to significantly reduce nitrate concentrations especially with both components providing bacteria. Non-sterile substrates did contain denitrifying bacteria. In 2 out of 3 experiments, the presence of dog food reduced the induction periods needed to form an active microbial population by about half, particularly at high nitrate concentrations. With pecan shells alone, the experiments with high nitrate concentrations required about twice as long as those with low nitrate concentrations to reduce nitrate levels to half the initial concentrations.

The results demonstrate that a healthy microbial population with denitrifying activity was established that can reduce even high nitrate concentrations to undetectable levels within about 1 week with the pecan shell/dog food combination, and in about twice that time without the dog food. As will be seen below, the Apatite II has sufficient residual organics to serve as a readily accessible food source to the adjacent biobarrier so that no additional food source is needed. The rate of denitrification will be adequate to reduce nitrate in the proposed multiple PRB for Mortandad Canyon given the flow rates and proposed dimensions.

B. COLUMN STUDIES

1. Pecan Shells with ^{87}Sr, NO_3^-, and Polystyrene Colloids

A single column study was undertaken to determine if pecan shells are a feasible material for the biobarrier part of the multiple PRB for degradation of nitrate. ^{87}Sr and colloids were also included to observe their behavior. The ground water was spiked with 2 mg/L ^{87}Sr, 50 mg/L $NaNO_3$ (for a total nitrate concentration of 100 mg/L) and

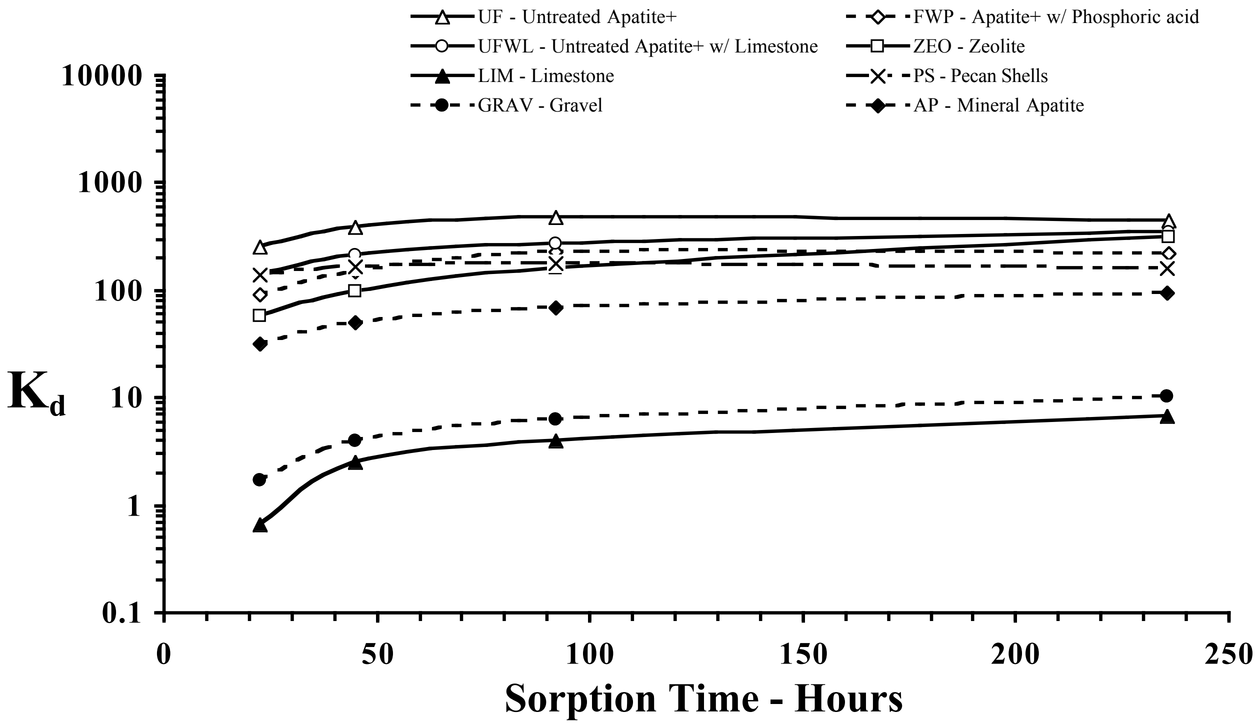


Figure 7. Sorption of Sr-85 Over a Ten Day Time Span

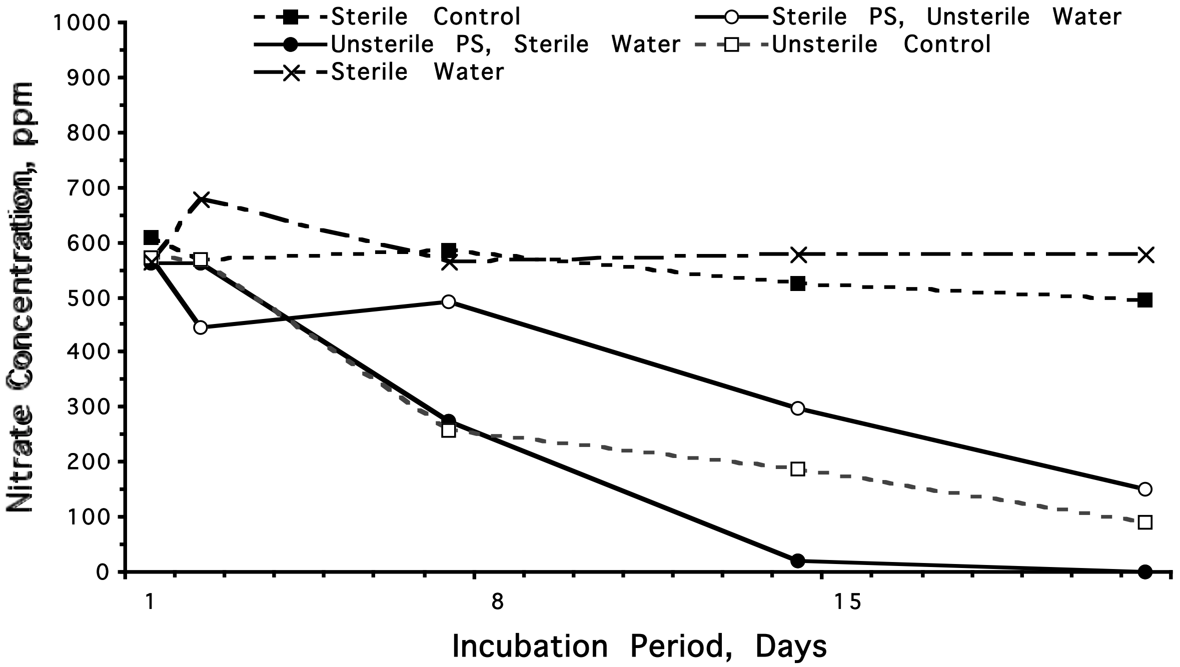


Figure 8. Nitrate Removal Over a Twenty-One Day Period

2x10^8 fluorescent colloids per L of water. ^{87}Sr was removed to below detection limits throughout the course of the experiment, an unexpected advantageous result. Nitrate concentrations initially appeared to be reduced, however, they reached a maximum concentration of 60 mg/L and decreased with time to approximately 30 mg/L. This incomplete removal of nitrate probably resulted from insufficient time being provided to establish an active microbial community, and no food source being available. Only eight pore volumes were put through the column, which at the 0.13 mL/min flow-rate took just over two days. As was seen later in column tests with Apatite II upstream of the pecan shells, the presence of an available food source from the Apatite II lead to rapid degradation of nitrate in the Apatite II. The pecan shells did not result in complete removal of colloids from the influent solution, however they did reduce the colloid concentration by at least an order-of-magnitude, providing evidence that pecan shells could serve as a secondary trap for retention of colloids that may escape the primary colloid barrier material. The average pH of collected effluents was 6.92 ± 0.10 and the average dissolved oxygen (DO) concentrations were 4.91 ± 0.12 mg/L.

It is difficult to compare the results for the pecan shells between the batch and column tests because the conditions are so different. The water to substrate ratio is much greater in the batch tests, and the residence time in the batch tests were much longer (21 day incubation times in the batch tests and only 2 days in the column tests). In the subsequent sequential column tests with all layers, the nitrate was unexpectedly removed by the Apatite II layer and so the performance of the pecan shells with respect to the nitrate could not be evaluated in a long-term column study.

2. Sequential Column Tests with ^{87}Sr and Nitrate

Mortandad Canyon ground water retrieved from well MCO-5 was spiked with 2 mg/L ^{87}Sr and introduced to the columns at a constant flow rate of 0.2 mL/min. Nitrate concentrations in the water from well MCO-5 were measured to be approximately 50 mg/L, therefore no additional nitrate was added to the ground water at first, but nitrate concentrations were increased to 205 mg/L in the influent on 4/14/00 (see Figure 10). Four columns, approximately 10 cm long with 4.8 cm inside diameter and loaded with the reactive media, were arranged in series as depicted in Figure 9. Column 1 was loaded with Catfloc coated gravel (0.5 L of 2 g/L Catfloc solution contacted with 280 g of gravel for 12 hours), column 2 with Apatite II pre-washed with hot water, column 3 with crushed pecan shells mixed with dog food to enhance microbial proliferation, and column 4 with limestone. Pore volumes were about 70 ml for each column and water residence times were about six hours for each of the columns. Three-way valves were placed between columns so that samples could be collected following contact with each reactive medium. Approximately 5.5 mL aliquots were retrieved manually at regular time periods between the columns while an Isco Foxy Junior fraction collector collected effluent from column 4 following complete treatment through the column sequence. ICP analysis of ^{87}Sr and nitrate ion chromatography ensued following collection of effluent from the columns.

Figure 10 illustrates ^{87}Sr and nitrate concentrations detected in the effluent following treatment through all four columns. Nitrate was removed to below detection limits throughout the course of the study except on the day that the concentration was increased to 205 mg/L, after which it dropped to below detection limits for the rest of the experiment. ^{87}Sr concentrations rarely exceeded the 0.85 mg/L leached baseline value of the Apatite II. The pH and dissolved oxygen (DO) concentration were monitored daily for each of the four columns. A comparison of average pH and DO concentration values, along with the influent water from well MCO-5, is presented in Table 4.

Table 4. MCO-5 water pH and DO concentration values, and daily average pH and DO concentration values individual columns.

Source Description	pH	DO (mg/L)
MCO-5 well water	8.03 ± 0.27	6.34 ± 0.20
Column 1 (Catfloc coated gravel)	7.82 ± 0.36	5.34 ± 0.15
Column 2 (Apatite II)	6.96 ± 0.11	1.89 ± 0.17
Column 3 (pecan shells + dog food)	6.47 ± 0.30	2.35 ± 0.20
Column 4 (limestone)	6.94 ± 0.19	2.00 ± 0.13

CATFLOC Coated gravel **Apatite II** **Pecan Shells** **Limestone gravel**

Figure 9. Sequential column tests of multiple PRB for Mortandad Canyon.

It appears from the DO concentrations that the Apatite II and its inherent residual organics was supporting a sufficient denitrifying microbial population to explain the removal of nitrate from solutions exiting the Apatite II. The pH results in Table 4 are consistent with the observation that apatite minerals buffer the pH to about neutral. The pecan shells and limestone do not have much effect in this column study because of the removal of nitrate by the Apatite II and the buffering effect of the Apatite II. There was concern that the limestone would raise the pH back towards 8, but the water residence time in the coarse limestone gravel is probably not long enough. Again the experiment was interrupted before breakthrough occurred.

3. Sequential Column Tests with ^{239}Pu, ^{241}Am, ^{85}Sr, Nitrate, and Perchlorate

Four aggregates were chosen for use in the 4 sequential columns in this test (Figure 11, Table 5). A 100 mL pulse of MCO-5 water spiked with 7×10^{-9} *M* ^{85}Sr, 5×10^{-7} *M* ^{239}Pu (750,000 pCi) and 1×10^{-9} *M* ^{241}Am was injected into the columns after the two-week equilibration period. The use of ^{85}Sr avoided the leaching problem of ^{87}Sr in the determination of total strontium sorption in this column test. As stated earlier, these radionuclide concentrations

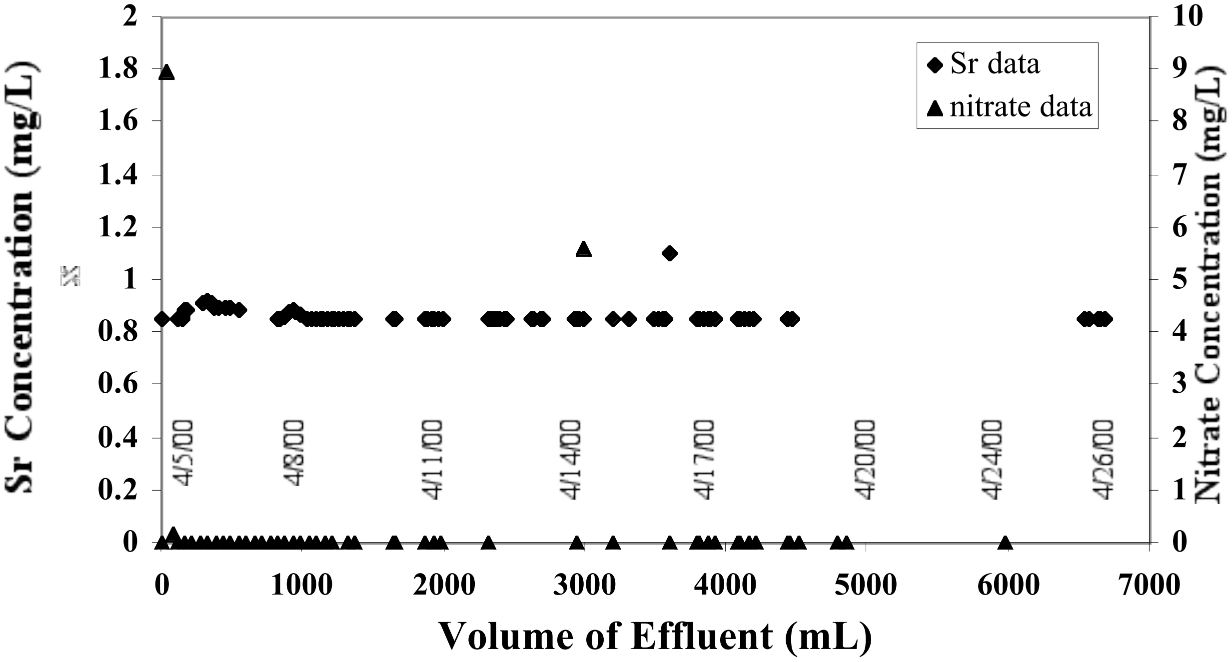


Figure 10. ^{87}Sr and nitrate concentrations in the final effluent from the sequential column study.

represent about 60 years of flow at present plutonium concentrations, 44 years of flow at present ^{90}Sr concentrations, and 10 years of flow at present ^{241}Am concentrations. Nitrate and perchlorate were at the field concentrations of 3.9 mg/L and 0.4 mg/L, respectively. No colloids were injected as part of this test. Relating a high-concentration pulse to long-term flow at lower concentrations is valid only if there is no degradation of removal efficiency of the solid over this time period.

Analysis of column elutants was conducted for three months until the experiment was interrupted. After injection of the contaminant pulse, approximately 300 pore volumes exited the columns with no detectable nitrate, perchlorate, plutonium, americium, or strontium (neither ^{85}Sr nor ^{87}Sr; no ^{85}Sr exited the Apatite II and no ^{87}Sr leached from the Apatite II exited the pecan shells), in the effluent. The immobilized plutonium, americium, and strontium, therefore, appear stable against future subsequent flow, at least for this number of pore volumes, a condition that needs to be addressed if the spent barrier materials need to be left in place after the plume is treated.

Table 5. Column Volumes and Masses.

Media	column 1 Catfloc treated volcanic rock	column 2 Apatite II	column 3 Pecan Shells	column 4 Limestone
Aggregate Dry Mass (g)	1910	2722	1510	8663
Pore Volume (mL)	3217	2705	3125	2304

Figure 11. Feasibility column network

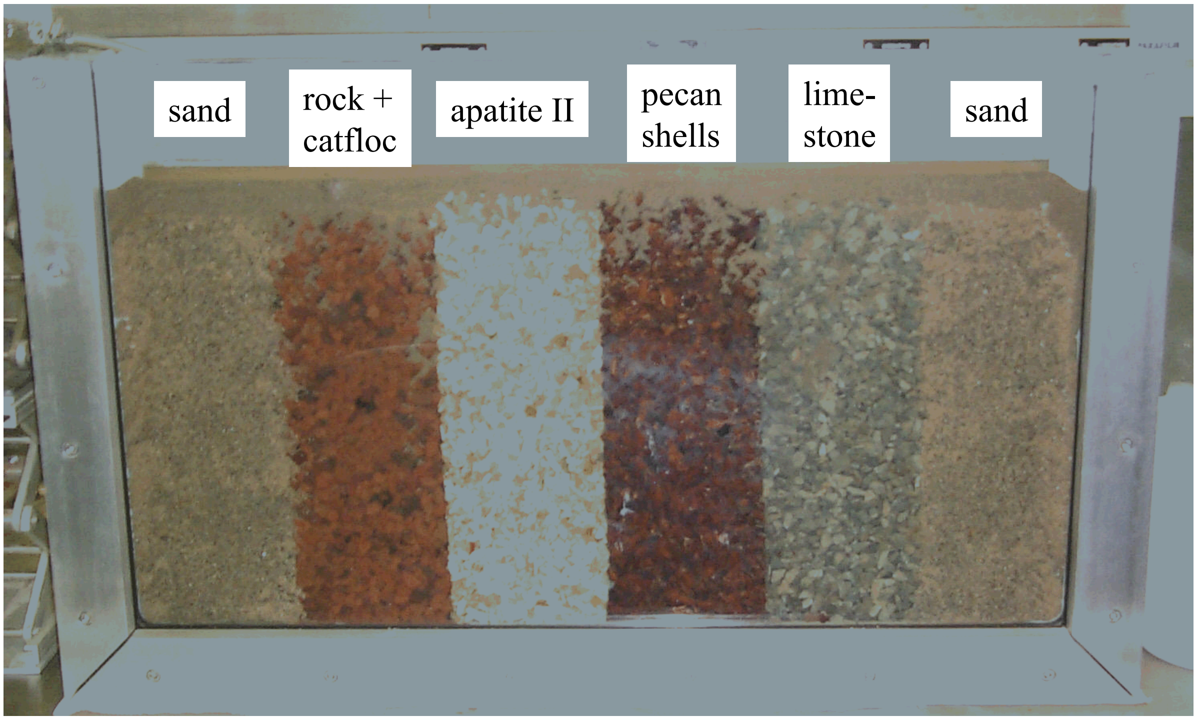


Figure 12. 2-D aquifer cell for treatment demonstration of contaminated groundwater.

4. 2-D Aquifer Box Tests with ^{87}Sr, Nitrate, and Perchlorate

A 2-dimensional (2-D) aquifer cell was assembled and loaded with basalt coated with Catfloc, Apatite II, pecan shells and limestone arranged in sequential vertical layers between sand similar to that in the field design (Figure 12). ^{87}Sr and perchlorate in water from well MCO-5 were injected in a constant concentration of 2 mg/L and 300 µg/L, respectively. Nitrate was injected at a constant concentration of 125 mg/L until day 60 when it was increased to 250 mg/L to evaluate the ability of microorganisms in the PRB materials to reduce irregular nitrate concentrations. With the flow rate of about 85 mL/hour and a total cell pore volume of about 2 L, the water residence time was about 1 day, the same as that observed in Mortandad Canyon shallow groundwater (1 pore volume per day).

Results were obtained for 100 days of continuous contaminant injection. Figure 13 shows the results exiting the aquifer box test after passing through all layers. The cell was constructed to allow discrete sampling between each layer interface. Samples taken between the first sand layer and the volcanic gravel (layer 1) and the volcanic rock and Apatite II (layer 2) showed no measurable change in a concentration for any of the contaminants. Effluents from all other layers showed the same results as in Figure 13, i.e., the Apatite II determined the contaminant concentration for all effluent. As was seen in previous tests, ^{87}Sr was leached from Apatite II at constant concentration of 0.85 mg/L and was not significantly reduced by passage through the remaining layers after the first week. All effluents following the Apatite II showed a strontium concentration of about 0.85 mg/L. The Apatite II layer reduced the nitrate and the perchlorate before entering the pecan shells to below detection limits in almost all samples. Detection limits for perchlorate were 3 µg/L (ppb).

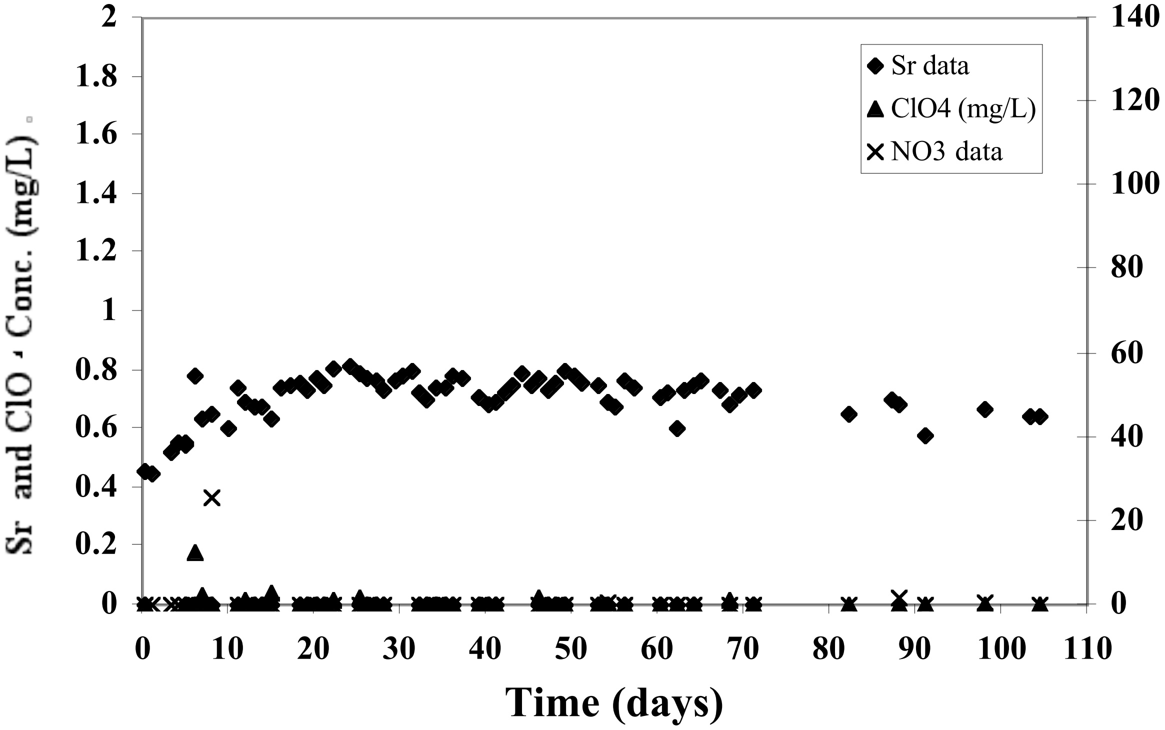


Figure 13. Effluent concentrations for strontium, nitrate and perchlorate exiting the multiple PRB in the aquifer test.

IV. CONCLUSION

The feasibility studies performed, thus far, indicate that a multiple PRB composed of four layers in sequence**,** Catfloc-coated volcanic gravel, Apatite II, pecan shells, and limestone gravel, could remediate shallow ground water at Mortandad Canyon, contaminated with ^{238,239,240}Pu, ^{241}Am, ^{90}Sr, nitrate and perchlorate, sufficiently to meet regulatory concerns. However, the performance period cannot be determined from the existing results because the feasibility studies were not able to result in breakthrough over the time periods of the study. Feasibility column tests for all contaminants, using ^{85}Sr, should be run to completion, or breakthrough, prior to installation in the field. Because the materials used are inexpensive, a large amount can be used to ensure conservative performance. If the barrier performs as well as desired in the field, the total expected inventory of radionuclides in the shallow aquifer is low enough that complete removal by so many tons of barrier material will not result in activities high enough for the barrier to become a hazardous or radioactive waste. The nitrate and perchlorate are reduced to harmless components and also will not cause the barrier to become a hazardous waste. Therefore, the materials could be left in place as long as regulatory approval could be obtained.

V. REFERENCES

Abdel-Fattah, A. I. and Reimus, P. W. 2000. in "Colloid attachment and detachment kinetics from direct visualization experiments" Report to the U.S. Department of Energy, Nevada Operation Office/Underground Test Area (UGTA) Program, April 2000.

Abdelouas, A., Lu, Y.M., Lutze, W. and Nuttall, H.E. 1998a. Reduction of U(VI) to U(IV) by Indigenous Bacteria in Contaminated Ground Water. *Journal of Contaminant Hydrology*, 35, 217-233.

Abdelouas, A., Lutze, W. and Nuttall, H.E. 1998b. Reduction of Nitrate and Uranium by Indigenous Bacteria. *Journal of the French Academy of Sciences* (*Comptes Rendus de L'Academie des Sciences, Serie II Fascicule A-Sciences de la Terre et des Planetes*) 327, 25-29.

Attaway, H. and Smith, M. 1993 Reduction of Perchlorate by an Anaerobic Enrichment Culture. *Journal of Industrial Microbiology*, 12, 408-412.

Benner, S.G., Blowes, D.W., Gould, W.D., Herbert, R.B.Jr. and Ptacek, C.J. 1999. Geochemistry of a permeable reactive barrier for metals and acid mine drainage. *Environmental Science and Technology*, 33, 2793-2799.

Benner, S.G., Blowes, D.W. and Ptacek, C.J. 1997. A Full-Scale Porous Reactive Wall for the Prevention of Acid Mine Drainage. *Ground Water Monitoring Review,* Fall 1997, 99-107.

Bowman, R.S. and Sullivan, E.J. 1995. Surfactant-modified zeolites as permeable barriers to organic and inorganic ground water contaminants, *in* "Proceedings, Environmental Technology Development through Industry Partnership Conference," 2, 392-397.

Blowes, D.W., Ptacek, C.J. and Jambor, J.L. 1997. In-situ remediation of Cr(VI)-contaminated ground water using permeable reactive walls: Laboratory studies. *Environmental Science and Technology*, 31, 3348-3357.

Bostick, W.D., Jarabek, R.J., Bostick, D.A. and Conca, J. 1999. Phosphate-Induced Metal Stabilization: Use of Apatite and Bone Char for the Removal of Soluble Radionuclides in Authentic and Simulated DOE Ground waters. *Advances in Environmental Research*, 3, 488-498.

Chen, X.-B., Wright, J.V., Conca, J.L. and Peurrung, L.M. 1997. Evaluation of Heavy Metal Remediation Using Mineral Apatite. *Water, Air and Soil Pollution*, 98, 57-78.

Collins, C.H., Lyne, P.M., and Grange, J.M. 1995. Microbiological Methods, 7th edition, Butterworth-Heinemann Ltd., publishers, Oxford, UK.

Conca, J.L. 1997. Phosphate-Induced Metal Stabilization (PIMS), Final Report to the U. S. Environmental Protection Agency #68D60023, Res. Triangle Park, NC.

Conca, J.L., Lu, N., Parker, G., Moore, B., Adams, A., Wright, J.V. and Heller, P. 2000. PIMS – Remediation of Metal Contaminated Waters and Soils, *in* "Remediation of Chlorinated and Recalcitrant Compounds" (G.B. Wickramanayake, A.R. Gavaskar and A. Chen, eds.) Battelle Memorial Institute, Columbus, Ohio, 7, 319-326.

Fruchter, J.S. 1996. In Situ Redox Manipulation Field Injection Test Report - Hanford 100 H Area, Pacific Northwest National Laboratory Technical Report PNNL-11372, Richland, WA.

Geochem Software Inc. 1994. Mac MINTEQ-A2: Aqueous Geochemistry for the MacIntosh, Published by Geochem Software, Inc., Reston, VA.

Goldstein, K.J., O'Hannesin, S., McDonald, S., Gaule, C., Anderson, G.A., Marsh, R. and Senick, M. 2000. Dual Permeable Reactive Barrier Walls Remediate Chlorinated Hydrocarbon Contamination, *in* "Remediation of Chlorinated and Recalcitrant Compounds" (Wickramanayake, Gavaskar, Gibbs and Means, eds.) Battelle Memorial Institute, Columbus, Ohio, 6, 273-280.

Herman, D.C. and Frankenberger, W.T.Jr. 1998. Microbial-Mediated Reduction of Perchlorate in Ground water. *Journal of Environmental Quality,* 27, 750-754.

Hocking, G, Wells, S.L. and Ospina, R.I. 2000. Deep Reactive Barriers for Remediation of VOCs and Heavy Metals. , *in* "Remediation of Chlorinated and Recalcitrant Compounds" (G.B. Wickramanayake, A.R. Gavaskar and A. Chen, eds.) Battelle Memorial Institute, Columbus, Ohio, 6, 307-314.

Kale, R.P.. 1993. Ground water Remediation Using Polyelectrolytes. M.S. thesis, Univ. of New Mexico.

Kersting, A.B.; Efurd, D.W.; Finnegan, D.L.; Rokop, D.J.; Smith, D.K.; and Thompson, J.L. 1999. Migration of Plutonium in Groundwater at the Nevada Test Site. *Nature*, 397, 56–59.

Lower, S.K., Maurice, P.A., Traina, S.J., and Carlson, E.H. 1998. Aqueous Pb sorption by hydroxylapatite: Applications of atomic force microscopy to dissolution, nucleation and growth studies. *American Mineralogist* 83, 147-158.

LANL. 1997. Work Plan for Mortandad Canyon, LA-UR-97-3291, Los Alamos National Laboratory, Los Alamos, NM 87545.

Ma, Q.Y., Traina, S.J. and Logan, T.J. 1993. In Situ Lead Immobilization by Apatite. *Environmental Science and Technology*, 27, 1803-1810.

Moody, T.E., and Wright, J. 1995. Adsorption Isotherms: North Carolina Apatite Induced Precipitation of Lead, Zinc, Manganese and Cadmium from Bunker Hill 4000 Soil, Technical Report BHI-00197, Bechtel Hanford, Richland, WA.

Moody, T.E. and Wright, J.V. 1996. Permeable Barrier Materials for Strontium Immobilization, Bechtel Hanford Technical Report BHI-00857, Bechtel Hanford, Inc., Richland, WA.

Morkin, M, Devlin, J.F., Barker J.F. and Butler B.J. 2000. In situ sequential treatment of a mixed contaminant plume. *Journal of Contaminant Hydrology*, 45, 283-302.

Naftz, D.L., Fuller, C.C., Davis, J.A., Piana, M.J., Morrison, S.J., Freethey, G.W., and Rowland, R.C. 2000. Field Demonstration of PRBs to Control Uranium Contamination in Ground water, *in* "Remediation of Chlorinated and Recalcitrant Compounds" (G.B. Wickramanayake, A.R. Gavaskar and A. Chen, eds.) Battelle Memorial Institute, Columbus, Ohio, 6, 281-290.

Puls, R.W., Blowes, D.W. and Gillham, R.W. 1999. Long-term performance monitoring for a permeable reactive barrier at the U.S. Coast Guard Support Center, Elizabeth City, North Carolina. *Journal of Hazardous Materials,* 68, 109-124.

Runde, W. 1992. The Chemical Interactions of Actinides in the Environment. *Los Alamos Science*. 26, 338-357.

Runde, W.; Meinrath, G. and Kim, J.I. 1992. A Study of Solid-Liquid Phase Equilibria of Trivalent Lanthanide and Actinide Ions in Carbonate Systems. *Radiochimica Acta,* 58/59, 93–100.

Starr, R.C. and Cherry, J.A. 1994. In situ remediation of contaminated groundwater: the Funnel-and-Gate system. *Ground Water,* 32, 456-476.

Sullivan, E.J., Bowman, R.S. and Haggerty, G.M. 1994. Sorption of inorganic oxyanions by surfactant-modified zeolites, *in* "Spectrum 94, Proceedings of the Nuclear and Hazardous Waste Management International Topical Meeting," 2, 940-945.

Tratnyek, P.G., Johnson, T.L., Scherer, M.M. and Eykholt, G.R. 1997. Remediating ground water with zero-valent metals: Kinetic considerations in barrier design. *Ground Water Monitor. Remed.,* 17, 108-114.

Triay, I.R., Meijer, A., Cisneros, M.R., Miller, G.G., Mitchell, A.J., Ott, M.A., Hobart, D.E., Palmer, P.D., Perrin, R.E. and Aguilar, R.D. 1991. Sorption of Americium in Tuff and Pure Minerals Using Synthetic and Natural Ground waters. *Radiochimica Acta,* 52/53, 141–145.

Triay, I.R, Meijer, A., Conca, J.L., Kung, K.S., Rundberg, R.S. and Strietelmeier, B.A. .1997. Summary and Synthesis Report on Radionuclide Retardation for the Yucca Mountain Site Characterization Project, (R. C. Eckhardt, ed), Los Alamos National Laboratory Technical Report LA-13262-MS, Los Alamos, NM.

Wallace, W., Beshear, S., Willims, D., Hospadar, S. and Owens, M. 1998. Perchlorate Reduction by a Mixed Culture in an Up-Flow Anaerobic Fixed Bed Reactor. *J. Indust. Microbiol. Biotechnol.* 20, 126-131.

Waybrant, K.R., Blowes, D.W. and Ptacek, C.J. 1998. Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. *Environmental Science and Technology.* 32, 1972-1979.

Wickramanayake, G.B., Gavaskar, A.R. and Chen, S.C. 2000. Remediation of Chlorinated and Recalcitrant Compounds, vol. 6, Battelle Memorial Institute, Columbus, Ohio.

Williamson, D., Hoenke, K., Wyatt, J., Davis, A. and Anderson, J. 2000. Construction of a Funnel-and-Gate Treatment System for Pesticide-Contaminated Ground Water, *in* "Remediation of Chlorinated and Recalcitrant Compounds" (G.B. Wickramanayake, A.R. Gavaskar and A. Chen, eds.) Battelle Memorial Institute, Columbus, Ohio, 6, 257-264.

Wright, J.V., Peurrung, L.M., Moody, T.E., Conca, J.L., Chen, X., Didzerekis, P.P. and Wyse, E. 1995. In Situ Immobilization of Heavy metals in Apatite Mineral Formulations, Technical Report to the Strategic Environmental Research and Development Program, Department of Defense, PNL, Richland, WA.

Wright, J. 1990. Conodont apatite: structure and geochemistry, *in* "Metazoan Biomineralization: Patterns, Processes and Evolutionary Trends" (J. Carter, ed.), Van Nostrand Reinhold, New York, 445-459.

Wright, J., Conca, J.L., Repetski, J. and Clark, J. 1990. Microgeochemistry of some Lower Ordovician Cordylodans from Jilin, China, *in* "1st International Senckenberg Conference and 5th European Conodont Symposium (ECOS V) Contributions III" (W. Ziegler, ed.), Courier Forschungsinstitut Senckenberg, Frankfurt, Germany, 118, 307-332.

Wright, J., Schrader, H. and Holser, W.T. 1987. Paleoredox Variations in Ancient Oceans Recorded by Rare Earth Elements in Fossil Apatite. *Geoch. Cosmoch. Acta* 51, 631-644.

Zumft, W.G. 1997. Cell Biology and Molecular Basis of Denitrification. *Microbiol. Mol. Biol. Rev.,* 61, 533-616.