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The phosphate-based mineral phases Apatite II and bone char are shown to be effective for the removal of select heavy metal impurities in groundwater. The performance of select apatite-based products is compared with that of other candidate sorption media (including granular activated carbon and anion exchange resin) for the removal of soluble uranium ion in synthetic Department of Energy (DOE) Site groundwater supplemented with varying levels of interfering nitrate ion. Apatite has a greater affinity for U(VI), especially in the presence of nitrate ion, as evidenced by a larger value for the conditional distribution coefficient (Kd) in batch test experiments. Contact of uranyl nitrate solution with apatite is shown to produce highly insoluble mineral phases of the autunite group (calcium uranyl phosphate hydrates). The activity of soluble uranium in contact with excess Apatite II reagent is equivalent to ~ 2-3 μg/L (i.e., 2-3 parts per billion) uranium. We also show that Apatite II is effective for the removal of soluble cerium ion, a nonradiological surrogate used to mimic the behavior of plutonium and other actinides or transuranic elements.

Key words: apatite, sorption, precipitation, uranium, groundwater remediation, nitrate ion, bone char, phosphate minerals

INTRODUCTION

The potential leaching of soluble uranium (as toxic and radioactive metal complexes) into groundwater systems is an environmental concern at many sites supporting the nuclear fuel cycle (e.g., mining, milling, and component fabrication operations, as well as material utilization). As an example, the uranium-bearing mixed (radioactive and hazardous) wastes that were formerly disposed of in unlined trenches at the Y-12 Plant in Oak Ridge, Tennessee, operated for the U.S. Department of Energy, represent the primary risk contributor to the Bear Creek Valley watershed, due to the leaching of contaminants into shallow groundwater. The contaminants of principal concern at this site are soluble uranium and cadmium ions; nitrate ion and volatile organic compounds are also present.

Remediation activity is mandated to eliminate unacceptable risks to human health and the environment associated with these sources and pathways. The primary regulations governing environmental restoration at the Y-12 site are the National Environmental Policy Act, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), the Superfund Amendment Reauthorization Act, and the Resource Conservation and Recovery Act (RCRA). These regulations specify a protocol for identifying and evaluating remediation options, and establishing a record of decision for a

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preferred action.

The propagation of contaminant groundwater plumes may be controlled by several approaches. The source of the plume may be physically isolated from contact with the groundwater by installation of a low-permeability containment barrier around the source. In an alternative approach, a fine-grained medium that reacts with the contaminant(s) of interest may be augered into the soil surrounding the source; the medium reacts with the contaminants in the source leachate to accomplish *in-situ* treatment or fixation, minimizing further off-site migration. Contaminants are either degraded or else they are sorbed or precipitated in the near-source field. An ideal medium would effectively reduce the toxicity and/or bio-availability of the reacted contaminant.

When contaminants have already entered the groundwater, options may include conventional (and often relatively ineffectual) pump-and-treat strategies (1). More recently, the use of permeable reactive barriers, or treatment walls, has gained some favor, having the perceived advantages of reduced installation, operation and maintenance costs. In this approach, contaminants in a groundwater plume are degraded or removed as they percolate through the barrier or treatment trench medium, allowing the decontaminated water to continue its natural flow course. A system incorporating containment walls may be used to capture and "funnel" the groundwater stream into a permeable reactive "gate" for treatment and discharge.

The preferred early action identified in the Y-12 Bear Creek Valley Proposed Plan under CERCLA is to remove or stabilize select "hot spots" of known or suspect contaminated soil or debris, in order to minimize the migration of priority contaminants into areas that have not yet been heavily impacted. In addition, a treatment trench incorporating reactive medium has been installed in one impacted groundwater pathway.

The reactive medium of choice for use at the Y-12 site should be effective for the *in-situ* stabilization of both uranium and cadmium (priority pollutants), and should be minimally affected by the presence of nitrate ion, which is present in many of the site groundwater systems. In CERLA Phase I lab-scale treatability studies, several candidate media were evaluated for this application, including zero-valent iron, pelletized iron oxides, activated carbon, ion exchange resins, phosphate rock, and peat moss (2-6). Most of the media examined were at least somewhat effective for the removal of soluble uranium in water having low total dissolved solids (TDS), but all were adversely affected by water containing high levels of nitrate ion. Zero-valent iron (ZVI) was selected to demonstrate *in-situ* treatment of uranium in a low-TDS contamination pathway.

ZVI has been used in numerous applications for remediating groundwater contaminated with chlorinated hydrocarbons and some metals (7). The proposed mechanism(s) for soluble uranium removal by ZVI have been debated in the literature, and may include reductive precipitation and/or sorption of uranium complexes onto iron oxide corrosion products (4, 7-10). Although ZVI was very effective for removal of soluble uranium in short-term batch testing, it was appreciably less effective for this application in longer-term column tests (2). Examination of core samples of ZVI removed from the *in-situ* treatment trench installed at Y-12 after ~ 1.2 years of service demonstrated only modest uptake of uranium (localized maximum observed loading ~ 1,000 mg-U/Kg, with most media samples loaded to 1-100 mg-U/Kg; Bostick and Matheson, unpublished results). These results may reflect the relatively low flux of soluble uranium ($\leq$ 1 mg-U/L in the influent groundwater), coupled to extensive surface deposition of nonreactive mineral phases (calcite, etc.) that may interfere with ZVI surface-mediated reactions (sorption or reduction).

Other candidate media may be considered for future demonstrations for the removal of soluble uranium and other heavy metals from the Y-12 water systems. In this report, we use batch testing to compare the performance of apatite (a family of substituted calcium phosphate mineral phases) to that of select benchmark sorbent media for the removal of soluble uranium in authentic and synthetic Y-12 groundwater compositions.

In order to compare the relative effectiveness of these solid phase media for the removal of soluble uranium, we computed a conditional distribution coefficient, Kd, using the relationship:

$$Kd = S/C \qquad (1)$$

where S = mass of contaminant "sorbed" at equilibrium per mass of sorbent, and C = equilibrium concentration of soluble contaminant in the aqueous phase.

If C is given in g/mL, then Kd has the units mL/g. The value of Kd obtained from equilibrium batch testing can be used to roughly estimate the packed bed capacity or retardation factor, R_f (i.e., reactor breakthrough, in cumulative bed pore volumes passed), with the caveat that solute mass transport and reaction kinetics significantly affect the performance of actual dynamic flow reactors (11):

$$R_f = [1 + Kd(\rho_b/\theta)] \quad (2)$$

where

R_f = Maximum number of bed pore volumes that can be treated before breakthrough,

Kd = Conditional contaminant distribution coefficient (mL/g), determined from the sorption isotherm,

ρ_b = Packed bed density (g/mL),

θ = Total void fraction of the packed bed.

For Equation 2 to be strictly valid, the value of Kd must be derived from a linear isotherm, or else (for nonlinear sorption isotherms, in which the observed value for Kd is a function of concentration) it must be the empirical value of the Kd determined at a solute equilibrium concentration equal to the solute concentration at the influent to the packed bed.

Equation 1 is equivalent to the expression for a simple linear sorption isotherm, but Kd may not be a true "constant" for removal mechanisms that do not involve limited surface binding sites; an example of the latter is reductive precipitation, which can ideally involve the deposition of many monolayers of conductive species on the reactive metal surface.

The observed value for Kd is sensitive to the equilibrium solution pH value and the solution temperature. Uptake of the contaminant of interest may be diminished by the presence of interfering ions that can affect the solid phase (by competition for the same binding sites on the sorbent, or by altering the surface properties, e.g., by nonspecific deposition), or that react with the solute (to form soluble complexes with the contaminant of interest or alter its net ionic charge distribution).

For apatite-based media, the mechanisms for removal of heavy metal from solution can be complex, and the term "sorption" is used loosely to describe the deposition of metal ions from solution to coexisting apatite structures (12). The parameter Kd, computed from Equation 1, is used here simply as a figure of merit for comparing the performance of different media in a given water composition under defined laboratory testing conditions.

Apatite occurs as geologically stable natural phosphate mineral deposits and as the principal inorganic constituent of bone tissue. UFA Ventures (Richland, WA) has recently developed a reactive, inexpensive form of microporous apatite (known as Apatite II) for use in environmental applications (U.S. Patent Pending). This product has previously been used at relatively low loadings (e.g., as little as 1-2 wt%) as a soil amendment to effectively control the potential off-site migration of select heavy metals (including lead, zinc, and cadmium) at contaminated mining sites by the formation of highly insoluble mineral phases; the metals are sequestered by reaction with the apatite mineral host, and have very low bioavailability (12-14). For instance, soluble lead is rapidly transformed into the mineral pyromorphite ($Pb_5(PO_4)_3(OH,Cl)$), which is isostructural with apatite and can form solid solutions in the apatite phase (12-16).

Table 1. Solubilities of Some Metal-Phosphate Phases and Quartz.

Mineral Phase	**Solubility Product ($\log_{10} K_{sp}$)**
$Pb_5(PO_4)_3(OH,Cl)$	-76.5
$Sr_5(PO_4)_3(OH)$	-51.3
$Ca(UO_2)_2(PO_4)_2 \bullet 10H_2O$	-48
$Ca_5(PO_4)_3OH$	-44
$Zn_3(PO_4)_2$	-35.3
$Cd_3(PO_4)_2$	-32.6
$Am(PO_4)$	-24.8
$Pu(PO_4)$	-24.4
Quartz (SiO_2)	-4.0

Theoretical solubilities (expressed as the logarithm of the solubility product, K_{sp}) for some important metal-phosphate and other reference phases are presented in Table 1 (data from the EPA MINTEQA2 database). For reference, we present the thermodynamic estimates for the K_{sp} of *crystalline* hydroxyapatite ($Ca_5(PO_4)_3OH$), and also for quartz (SiO_2), a phase commonly regarded as being insoluble in water. It is noted that Apatite II reagent is poorly crystalline, and it is thus considerably more soluble than is crystalline hydroxyapatite. Experimental values for select soluble heavy metal ion concentrations in equilibrium with Apatite II reagent are typically in the low parts-per-billion (ppb) range; e.g., (from Wright *et al.* (13): Cd <5 ppb (<4.4E-8 mol/L); Pb <1 ppb (<0.5E-8 mol/L); Zn <1 ppb (<1.5E-8 mol/L); and (*vide infra*) U <3 ppb (<1.3E-8 mol/L).

Murray *et al.* (17) have demonstrated the use of synthetic apatite for the retention of uranium and its daughter products leached from wastes from a uranium mine; radium leach values were reduced to

Table 2. Select Characteristics of Y-12 Bear Creek Valley Groundwaters (Filtered with 0.45-um Media).

Property	NT-1	BYBY Water	
	Batch 2	GW-087, Batch 2	Synthetic BYBY[1]
pH (std. units)	5.80	6.72	~6.0-7.2
Alkalinity (total, as mg/L $CaCO_3$)	150	174	132
Conductivity (umhos/cm @ 25 C)	14,800	360	330
Total activity (pCi/L)	22,600	10	NA[2]
Chloride ion (mg/L)	258	16	20
Nitrite ion (mg/L)	52	<1	NA
Nitrate ion (mg/L)	12,400	<1	NA
Sulfate ion (mg/L)	50	21	24
Aluminum (mg/L)	0.96	0.08	NA
Barium (mg/L)	15	0.11	NA
Calcium (mg/L)	1,800	57	50
Cadmium (mg/L)	0.06	0.004	NA
Magnesium (mg/L)	400	5.1	6.0
Manganese (mg/L)	140	0.69	NA
Nickel (mg/L)	4.6	<0.0025	NA
Potassium (mg/L)	43	4	7.0
Sodium (mg/L)	640	<5	12
Uranium (mg/L)	0.008	0.24	NA

[1] See text for formulation; [2] NA indicates that component is not added.

very low levels (typically below 0.1 pCi/L). In recent testing performed at the University of New Mexico (18), various apatite products were demonstrated to be effective for the removal of soluble arsenic and the radionuclides uranium, plutonium, and americium supplemented into synthetic DOE Rocky Flats groundwater.

In the work presented here, we confirm that apatite mineral phases are highly reactive with soluble uranyl ion (UO_2^{2+}, or hexavalent uranium), producing highly stable, insoluble minerals of the autunite family (calcium uranyl phosphate hydrates); see Table 1.

EXPERIMENTAL

Water Samples

The Bear Creek Valley (BCV) Characterization Area at the Oak Ridge Y-12 Plant has several groundwater streams and seeps that may require remediation (3, 4). Water compositions characteristic of two of these priority streams were used in the experiments. The water used was representative of the so-called Boneyard/Burnyard (or BYBY) pathway water (typified by water from well GW-087) and water from North Tributary 1 (NT-1). Representative analytical data for these two distinct water types are given in Table 2; compared to the BYBY water, the NT-1 water has elevated concentrations of total dissolved solids (TDS), notably from calcium and nitrate ions, RCRA-regulated metals, and the radioisotope technetium-99 (^{99}Tc). The water samples, as-received, had relatively low concentrations of soluble uranium, and were supplemented for testing purposes with soluble uranyl ion, either from natural uranium or uranium enriched with the higher specific activity isotope ^{233}U.

We used MINTEQA2, a public-domain geochemical equilibrium speciation model, to predict that uranium carbonate species predominate at near-neutral pH values in these oxic water compositions (9); the neutral species UO_2CO_3 is predicted to predominate at pH values ~ 5.0 to 6.5, and the anionic species $UO_2(CO_3)_2^{2-}$ predominates over the pH range of ~ 6.5 to 8.5. In addition to affecting the uranium solute speciation, solution pH affects the net charge distribution on substrate surfaces, thus affecting the ability of a sorbent to attract and bind ionic solutes.

In additional testing, we prepared a synthetic surrogate to represent the BYBY water composition (10). The surrogate was prepared by the addition, per liter of deionized water, of the following chemicals: $MgSO_4 \bullet 7H_2O$, 61.1 mg; $CaCl_2 \bullet 2H_2O$, 41.1mg; $Ca(OH)_2$, 72 mg; $NaHCO_3$, 45 mg; and $K_2CO_3 \bullet 1.5H_2O$, 15.2 mg. Calcium ion was solubilized, and pH adjusted, by sparging the solution overnight with a gas mixture comprised of 80% N_2 and 20% CO_2. The pH after sparging was initially ~ 6.0, but gradually increased to >7 after several days of storage, as the solution equilibrated with ambient air. (Authentic GW-087 water behaves similarly, as excess CO_2 is lost). The nominal composition of synthetic BYBY water is given in Table 2. Surrogate material (synthetic BYBY water) was also supplemented with sodium nitrate to simulate the NT-1 type water. These synthetic water samples were traced with ^{233}U.

Measurement of Radiation in ^{233}U-Traced Solutions

Uranium oxide (as U_3O_8), enriched in isotope ^{233}U, was obtained from the Oak Ridge Y-12 Plant; the oxide was dissolved in a minimal amount of ultrapure nitric acid, and diluted to a known volume to provide a stock tracer solution (5.78 mg U/mL). The decay series for ^{233}U and daughters produces α, β, and γ radiation:

$$^{233}U \text{ -> } {}^{229}Th + \alpha + \gamma \text{ -> } {}^{225}Ra + \alpha + \gamma \text{ -> }$$

$$^{225}Ac + \beta + \gamma, \text{ -> ..... -> } {}^{209}Bi \quad (3)$$

The α and β radiation components of the decay series were measured by placing an aliquot of dilute solution in a scintillation cocktail (e.g., Ecolite (ICN, Costa Mesa, CA) or Ultima Gold (Packard Instruments, Meriden, CT)), and counted with use of a liquid scintillation counter (LSC; Packard Instruments 2550 Tri-Carb Liquid Scintillation Analyzer). In the presence of relatively high ^{99}Tc (which produces interfering β activity), the γ activities of ^{233}U and daughters were selectively monitored with use of a Packard Auto-Gamma 500C radiation measurement system. Both counting systems gave responses that were linear with tracer concentration, but, with our instrumentation, the LSC was more sensitive by a factor of >60; by LSC, one microgram (μg) of traced uranium gave a response of ~21,700 counts per minute (CPM), allowing precise estimates of small residual concentrations (e.g., low ppb) of U and its decay daughters.

Batch Equilibration Testing

In a typical batch test, a small, known quantity of solid-phase medium (e.g., ~ 50 ± 2 mg) and a known volume of test solution (10 mL) were contacted in a sealed glass vial for 16-24 h, with use of a Burrell wrist-action shaker (Burrell Scientific, Pittsburgh, PA). After equilibration, the phases were separated using a disposable syringe fitted with a 0.2 μm filter membrane ("Acrodisc", Gelman Scientific, Ann Arbor, MI), and a measured mass or volume of filtered solution was counted for activity.

For some media, we tested soluble uranium removal efficiency over a range of solution pH values. To do this, a well-stirred 20 mL aliquot of test solution was adjusted to the target pH value with use of dilute nitric acid or sodium hydroxide. Small aliquots of the pH-adjusted solution, with and without filtration, were reserved for counting; the unfiltered aliquot was used to determine the initial activity, Co, whereas the filtered aliquot was used to account for nonspecific losses (e.g., hydrolysis of uranium complexes at higher pH values). A 10 mL aliquot of the pH-adjusted solution was added to a scintillation vial containing ~ 50 mg of solid phase medium, and equilibrated as described above. The final equilibrium pH value was recorded, along with the fraction of residual soluble uranium (C/Co).

In a separate qualitative demonstration, Apatite II product was contacted by shaking it with a uranyl nitrate solution at an initial pH value ~ 3. After ~ 2 h contact time, the denser solids were allowed to settle, and the fines were decanted off. The dense solids were washed twice by resuspension in distilled water followed by decanting away the fines. The solid residue was then dried at 110 °C, and examined by X-ray powder diffraction to identify crystalline phase(s) formed.

We performed a similar qualitative test using Apatite II and Ce^{+3} ion, a nonradiological lanthanide group element, often used as a surrogate to mimic the behavior of trivalent actinides and plutonium (19, 20). A slight nominal stoichiometric excess (~30%) of Apatite II was contacted with 0.05 mol/L cerium nitrate solution by shaking overnight. Again, the "light" fraction was decanted by washing the product in deionized water.

Media Tested

Charcoal. Mersorb-3 (from Nuclear Consulting Services, Inc., Columbus OH) was selected as a representative charcoal product, having performed moderately well for the removal of soluble radionuclides from authentic site water samples in preliminary testing (4). This product is impregnated with ~ 10 wt% sulfur.

Bone Char. The inorganic component of bone is essentially a hydroxyapatite structure $[Ca_4(CaOH)(PO_4)_3]$; at 1100 to 1600 °F (~600 to 870 °C), bone is thermally degraded to yield a typical composition of $Ca_3(PO_4)_2$ (~ 74%), with residual $Ca(CO_3)_2$ (~ 8%), carbon (~9%), and trace mineral phases, such as iron and aluminum oxides (21). The skeletal structure of calcium phosphates has a great number of minute pores which are coated with finely-divided active carbon.

In this work, a typical commercial product was used: EM Science (Gibbstown, NJ) animal charcoal, product no. CX0635, with a nominal composition of ~ 88% tricalcium phosphate and ~ 12% carbon. This product is supplied as a very fine powder (B.E.T. surface area ~ 82 m^2/g). We also tested prototype materials prepared by Cercona of America (Dayton, OH). A bone char material was prepared by coking bone meal with an organic binder at ~ 800 °C to form beaded agglomerates (sized to ~ 8/12 mesh); this material was noted to have relatively modest crush-resistance. A second material was prepared using a proprietary aluminum phosphate binder; raw bone meal and binder were calcined in the absence of air (i.e., coked) at 1000 °C. This material had much improved crush-resistance.

Apatite. Hydroxyapatite and its carbonated analog $(Ca_{10}(PO_4)_5(CO_3)(OH)_2)$ are the principal mineral components of bone tissue, and apatite mineral deposits also occur naturally in the geosphere. Apatite II$^{(TM)}$ is a reactive form of apatite, supplied by UFA Ventures, Inc. (Richland, WA); this material is provided as a fine powder, with B.E.T. surface area ~ 1.9 m^2/g. A coarser grade of material (ca. -8/+20 mesh), designated Apatite III, with a surface area of ~ 0.16 m^2/g was also used. We also tested a synthetic apatite derivative, cool white lamp phosphor, provided courtesy of General Electric Chemical Products Operations (Cleveland, OH). This high surface area phosphor (particle size ~ 2-10 µm), used in the manufacture of fluorescent lamps, is an apatite partially substituted with fluoride ion.

Table 3. Estimated Parameters for Select Media.

Medium	B.E.T. Surface Area (m^2/g)	(ρ_b/θ), g/mL	$U.S./ton (est.)
Apatite II	1.9	NE	500
Apatite III	0.16	1.6	500
EM Bone Char	82	NE	2,000
Chabazite	NE	1.0	2,800
Mersorb-3	767	1.3	NE
Dowex 2-X8	NE	1.6	15,000

NE = parameter not estimated

Anion Exchange Medium. Dowex^{TM} 2-X8 resin (Bio-Rad laboratories, Richmond, CA) is a Type 2 strongly basic anion exchange resin that has appreciable selectivity for anionic uranyl carbonate complexes (22).

Chabazite. Chabazite (Product TSM-300, Steelhead Specialty Minerals, Spokane, WA) is an aluminosilicate zeolite material with the approximate composition $(Ca, Na_2)Al_2(SiO_3)_6 \bullet 6H_2O$.

Some estimated parameters for select treatment media are presented in Table 3. Bulk material costs are estimated in $U.S. per short ton of material. These estimates are approximations at the time that this document was prepared; current bulk material costs are subject to market factors, and the reported values are given for comparative purposes only. The ratio (ρ_b/θ) relates to Equation 2, for estimation of retardation factor.

RESULTS AND DISCUSSION

Figure 1 illustrates the pH-dependency of the conditional distribution coefficient (Kd) for soluble uranium, as monitored for ^{233}U traced into BYBY-type water from well GW-087 (low TDS), based on experiments using bone char media. Specific "sorption" (or, more precisely, mediated removal of contaminant) was greatest at slightly acidic to near-neutral pH values (pH ~ 4 to 8). Note that soluble uranium was still effectively removed at pH >8, but the predominant mechanisms are presumably hydrolysis and precipitation of insoluble polynuclear uranate complexes, not necessarily mediated by the bone char medium (i.e., at elevated pH values, the proportion of total uranium that is soluble is greatly diminished,

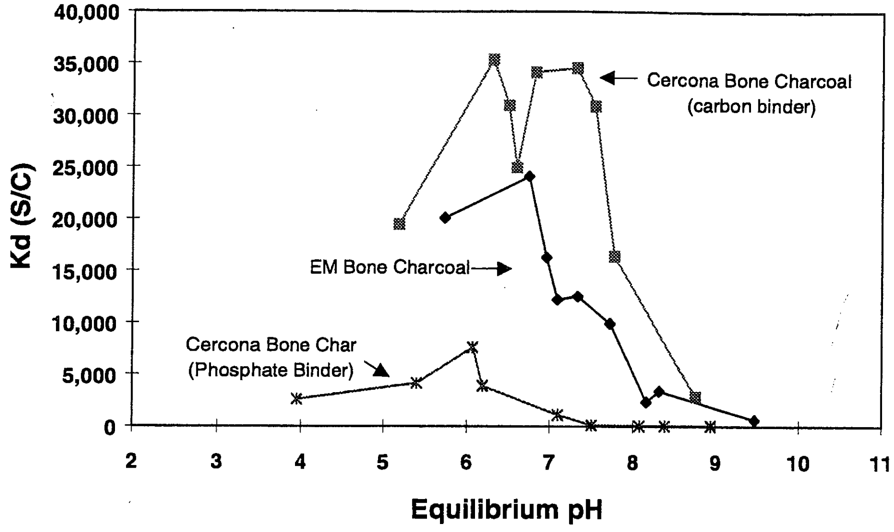

Figure 1. Comparison between EM and Cercona Bone Charcoals in ^{233}U Spiked Well 087 Batch 2 (BYBY Water).

even without treatment medium). Cercona bone char material (carbon binder) was appreciably more effective than the commercial EM bone charcoal for removal of soluble uranium; however, incorporating the Cercona bone char into an aluminum phosphate binder dramatically decreased its effectiveness. The latter behaved comparably in effectiveness for uranium removal to the natural phosphate rock material evaluated by Klasson *et al.* (5). Gu *et al.* (6) also evaluated the Cercona bone char in aluminum phosphate binder for removal of uranium, and found it to be intermediate in effectiveness between research grade peat moss and Cercona pelletized iron oxide.

Figure 2 presents corresponding data for the EM bone charcoal material in NT-1 water (containing ~12,400 ppm nitrate ion; see Table 2). The ^{99}Tc activity was monitored in untraced NT-1 water by the LSC technique, whereas gamma counting was used to selectively monitor added ^{233}U tracer in a separate series of experiments. The modest, pH-dependent removal of ^{99}Tc (present as the pertechnetate anion, TcO_4^-) is attributed primarily to anion exchange (as inferred from the interference by added nitrate ion) and nonspecific sorptive properties of the bone char material.

The pH-dependent selective removal of soluble U presented in Figure 2 follows the same trend as for the pertechnetate anion, although soluble uranium is expected to be present predominantly as cationic or neutral complexes for pH values below ~6 (9).

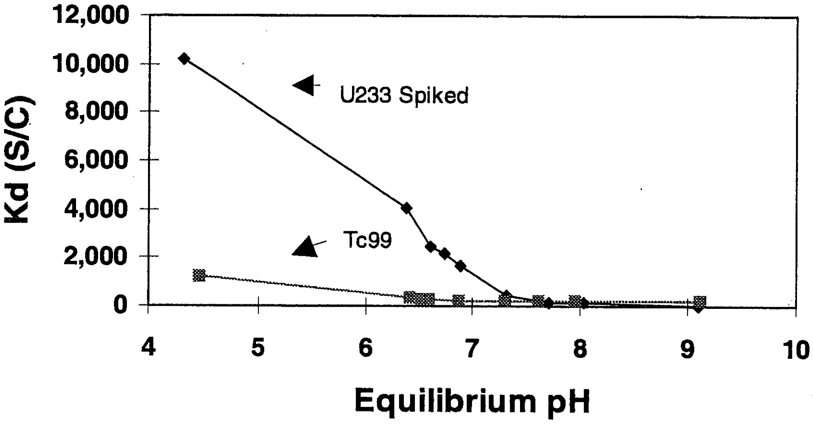

Figure 2. Comparison of U and ^{99}Tc Removal from NT-1 Batch 2 Using EM Bone Charcoal.

These data suggest that the bone char product tested may have both anionic and cationic binding sites, perhaps as an artifact of the conditions used to calcine the product. As noted previously, nonselective removal of soluble uranium does occur at pH >7, but predominantly by mechanisms not mediated by the bone char medium. A comparison of Figures 1 and 2 indicates that the selective removal of soluble uranium by bone char is significantly diminished in the NT-1 water composition (Figure 2), most likely due to the relatively high concentration of the nitrate anion, which interferes with the uptake of anionic uranyl carbonate complexes formed at higher pH values.

In Figure 3, we compare the performance of various solid-phase reagents for the removal of soluble uranyl ion added at 580 ppb to synthetic BYBY water, supplemented with different levels of nitrate ion. The UFA-V Apatite II product was the most effective reagent evaluated in this series of tests, and it demonstrated only a relatively modest reduction in Kd values in the presence of added nitrate ion. Ma and co-workers (15) similarly noted minimal interference by relatively high levels of common anions on the uptake of soluble lead by hydroxyapatite. The average residual soluble U activity after contact with the Apatite II material corresponded to ~2 ng/mL (or 2 ppb), a value comparable to the average concentration of U in seawater (~3 ppb) (23).

As expected, high levels of nitrate ion had the most pronounced and detrimental effect on the Dowex 2-X8 anion exchange resin, due to competition for the sorptive binding sites. Apatite II, bone charcoal, and Dowex resin were much more effective for the removal of soluble uranium than was chabazite (a natural zeolite, with cationic binding sites), Mersorb-3 charcoal, or synthetic lamp phosphor. The relatively poor performance of the synthetic phosphor product, relative to bone char or Apatite II, indicates that apatite minerals can vary greatly in their reactivity with heavy metals.

We investigated the effect of apatite medium particle size on the apparent kinetics for removal of soluble uranium in synthetic BYBY water, by comparing the performance of Apatite II (~1.9 m^2/g) and a similar product called Apatite III (~0.16 m^2/g); see Figure 4. The silt-like Apatite II material was readily suspended in solution with the wrist-action shaker (where it reacts rapidly with soluble uranium; see Figure 4), whereas the coarse Apatite III material remained at the bottom of the contact vessel. This difference in effective mass-transfer kinetics for contact mixing is apparent in the data for soluble uranium removal at short-term contact (<5 h), but at longer time (e.g., >33 h contact), the two materials

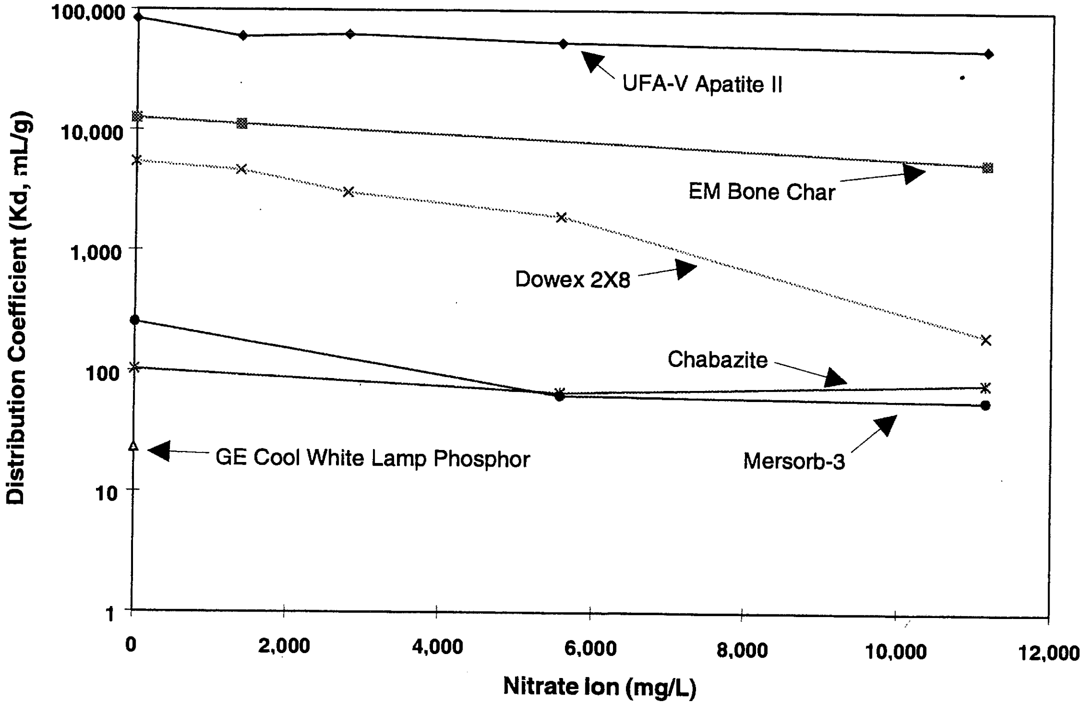

Figure 3. Effect of Nitrate Ion on Removal of Soluble Uranium (Co = 0.58 ppm U(VI) in Synthetic BYBY Water).

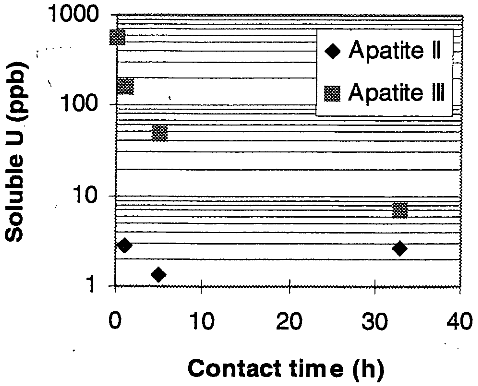

Figure 4. Removal of Soluble U from Synthetic Groundwater by Fine-Grain (Apatite II) and Coarse (Apatite III) Media. (Media dosage: 5 g/L; phases contacted with use of wrist-action shaker; phases separated with use of 0.2 μm filter medium).

perform similarly. Thus the coarser grade of apatite, with improved hydraulic conductivity properties, may be viable for use in a permeable reactive barrier or leachate treatment trench for the removal of soluble uranium or similar contaminants, given sufficient contact time. The improved phase contact should be able to overcome the mass-transport limitations suggested by the batch-testing data presented in Figure 4. In the presence of excess apatite, residual uranium activity is solubility-limited (to < 3 ng-U/mL, i.e., < 3 ppb). Further addition of Apatite II did not alter the residual uranium concentration, although the computed value for Kd decreased with increasing reagent dosage (since the residual uranium is limited by reaction product solubility, rather than by the saturation of available binding sites on the medium). It is noted that contact with apatite phase tends to buffer the solution to near-neutral values (pH 7 to 8).

The results indicate that silt-like Apatite II has potential for use as an admixture (with, e.g., native soil or bentonite clay) for waste repository backfill, to further reduce the risk of off-site migration of actinide or transuranic metals. Arey and coworkers (24) have recently shown that synthetic hydroxyapatite amendments, at dosages as little as 1 wt% in batch tests, effectively immobilized uranium in contaminated sediments, even in the presence of natural organic matter (NOM) that otherwise rendered an appreciable fraction of the uranium contamination highly leachable. McCarthy *et al.* (25) discuss the enhancing effect of NOM for the solubility and transport of actinide and transuranic elements, by analogy to the behavior of nonradiological lanthanide group surrogates.

Figure 5 presents the results of the X-ray diffraction of the solid residue obtained from the reaction of

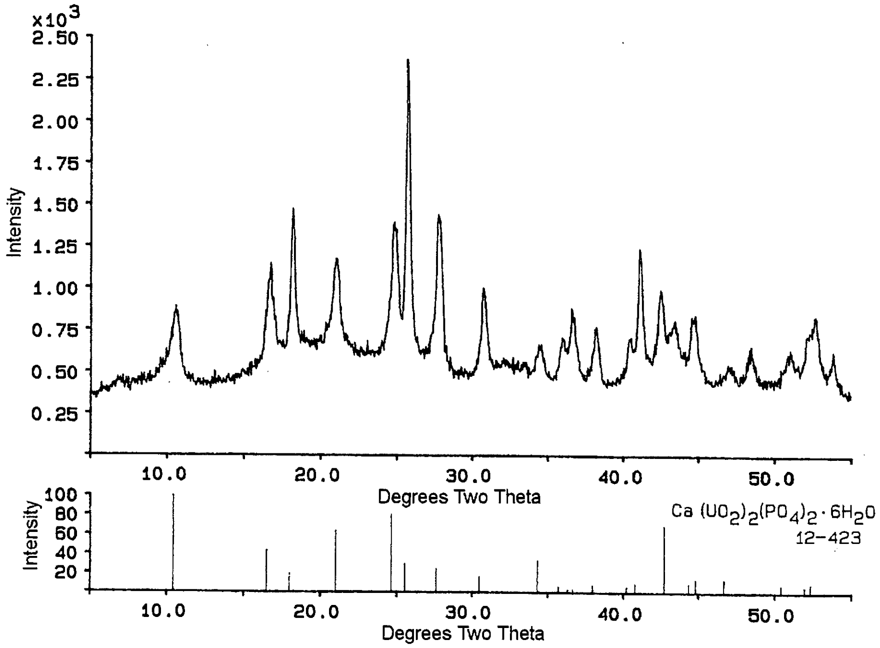

Figure 5. X-Ray Diffraction of Apatite II Reacted with Soluble Uranium. (Pattern matches ICCD file 12-423, Meta Autunite).

Apatite II with uranyl nitrate solution. The U-bearing crystalline phase was identified as meta-autunite ($Ca(UO_2)_2(PO_4)_2 \bullet 6.5H_2O$). It is possible that the precipitate originally contained autunite ($Ca(UO_2)_2(PO_4)_2 \bullet 10H_2O$), which was partially dehydrated during the product drying step (26). The dried solids were examined by X-ray fluorescence (XRF), and found to contain ~29 wt% U (cf. pure meta-autunite, ~54 wt% U).

For the test using Apatite II and Ce^{+3}, the dense residual product was largely amorphous (i.e., no distinct X-ray diffraction pattern, other than a small residual of unreacted apatite), but contained ~23 wt% as cerium, as estimated by XRF. On a molar basis, this cerium loading corresponds to ~34% of the total available phosphorous (based upon XRF estimates for both elements in the product).

CONCLUSIONS

Apatite II material is shown to be highly effective for the removal of uranium from aqueous solution. In agreement with previous observations for treatment of lead and other heavy metals, Apatite II is considerably more effective than the other phosphate reagents tested (compare to bone char in aluminum phosphate binder in Figure 1, or to lamp phosphor in Figure 2). Our data provide evidence that uranium is precipitated in the form of highly insoluble mineral phases of the autunite family (consistent with thermodynamic prediction, Table 1); autunite is geologically stable and is representative of some naturally occurring uranium-bearing ores.

Compared to the use of conventional sorbents, extremely high waste loadings (e.g., 20-30 wt %) are possible with apatite reagent, even in the presence of nitrate ion, which interferes with most sorptive mechanisms.

Further studies are warranted to explore the potential of Apatite II for use as an admixture for waste repository backfill, and Apatite III for use in a treatment trench or permeable reactive barrier configuration.

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REFERENCES

1. Nyer, E. K, 1996, "Limitations of Pump-and-Treat Remediation Methods", Chapt. 1 in In Situ Treatment Technology, Nyer, E. K. *et al.* (eds), Lewis Publishers, Boca Raton, FL.
2. Watson, D, Leavitt, M, Smith, C., Klasson, T, Bostick, B., Liyuan, L, Moss, D., 1997, Bear Creek Valley Characterization Area Mixed Wastes Passive In Situ Treatment Technology Demonstration Project - Status Report, in *Proc. Internat. Containment Conf*, St. Petersburg, FL, Feb. 9-12, 1997, pp. 730-736.
3. Science Applications International Corporation, 1997, Phase I Report on the Bear Creek Valley Treatability Study, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee, Lockheed Martin Energy Systems, Inc., Report Y/ER-285.
4. Bostick, W. D., Jarabek, R. J., Slover, W. A., Fiedor, J. N., Farrell, J, Helferich, R., 1996, Zero-Valent Iron and Metal Oxides for the Removal of Soluble Regulated Metals in Contaminated Groundwater at a DOE Site, Lockheed Martin Energy Systems, Inc., Report K/TSO-35P. (Included as Appendix D to Ref. 3).
5. Klasson, K. T., and Taylor, P. A., 1997, Bear Creek Valley Characterization Area Technology Demonstration Project: Sorption Studies, [Appendix B to Ref. 3].
6. Gu, B., Liang, L., Dickey, M. J., Yin, X., and Dai, S., 1998, Reductive Precipitation of Uranium(VI) by Zero-Valent Iron, *Environ. Sci. Technol.*, 32, 3366-3373.
7. Tratnyek, P., 1996, Putting Corrosion to Use: Remediating Contaminated Groundwater with Zero-Valent Metals, *Chemistry & Industry*, 1 July 1996, pp. 499-503.
8. Cantrell, K. J., Kaplan, D. I., and Weitsma, T. W., 1995, Zero-Valent Iron for In Situ Remediation of Selected Metals in Groundwater, *J. Haz. Mater.*, 42(2), 201-212.
9. Farrell, J., Bostick, W. D., Jarabek, R. J., and Fiedor, J. N., 1999, Effects of Water Chemistry on Uranium Removal from Groundwater Using Zero-Valent Iron Media, *Ground Water*, 37(4), 618-624.
10. Fiedor, J. N., Bostick, W. D., Jarabek, R. J., Farrell, J., Understanding the Mechanism of Uranium Removal from Groundwater by Zero-Valent Iron Using X-Ray Photoelectron Spectroscopy, 1998, *J. Environ. Sci. Technol.*, 32, 1466-1473.
11. Relyea, J. F., 1982, Theoretical and Experimental

Considerations for the Use of the Column Method for Determining Retardation Factors, *Radioactive Waste Management and the Nuclear Fuel Cycle*, 3(2), 151-166.

12. Chen, X.-B., Wright, J. V., Conca, J. L., and Peurrung, L. M., 1997, Effects of pH on Heavy Metal Sorption on Mineral Apatite, *Environ. Sci. Technol.*, 32(3), 624-631.
13. Wright, J. V., Peurrung, L. M, Moody, T. E., Conca, J. L., Chen, X., Didzerekis, P. P., 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, Pacific Northwest Laboratory, Richland, WA, 154 p.
14. 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(1-2), 57-78.
15. Ma, Q. Y., Logan, T. J., Traina, S. J., Ryan, J. A., 1994, Effects of NO_3^-, Cl^-, SO_4^{2-}, and CO_3^{2-} on Pb^{2+} Immobilization by Hydroxyapatite, *Environ. Sci. Technol.*, 28(3), 408-418.
16. Zhang, P, Ryan, J. A., Yang, J, 1998, In Vitro Soil Pb Solubility in the Presence of Hydroxyapatite, *Environ. Sci. Technol.*, 32(18), 2763-2768.
17. Murray, F. H., Brown, J. R., Fyfe, W. S., and Kronberg, B. I., 1983, Immobilization of U-Th-Ra in Mine Wastes by Phosphate Mineralization, *Canadian Mineralogist*, 21(4), 607-610.
18. Anderson, C. L., Thomson, B. M., Busch, R. D., Siegel, M. D., and Baldwin, C., 1998, Removal of Metals and Radionuclides Using Apatite and Other Natural Sorbents, Technical Completion Report to New Mexico Waste Management Education and Research Consortium.
19. Stockdale, J. A. D., Bostick, W. D., Hoffmann, D. P., Lee, H. T., 1994, Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste: Part I: Radiological Surrogates, Report DOE/MWIP-15, Martin Marietta Energy Systems, Inc.
20. Bates, S. O., 1993, Definition and Compositions of Standard Waste Streams for Evaluation of Buried Waste Integrated Demonstration Treatment Technologies, Report EGG-WTD-10660, Idaho National Engineering Laboratory.
21. Mantrell, C. L., 1951, "Bone Char", Chapt. 5 in Adsorption, 2nd ed., McGraw-Hill Book Co., New York, pp. 100-108.
22. Maya, L., 1981, Dioxo Uranium(VI) Carbonate Complexation in Uranium Recovery by Reactive Ion-Exchange, *J. Inorg. Nucl. Chem.* 43, 2133-2137.
23. Demayo, A., 1988, "Elements in Sea Water", in CRC Handbook of Chemistry and Physics, 68th Ed., CRC Press, p. F-142.
24. Arey, J. S., Seaman, J. C., and Bertsch, P. M., Immobilization of Uranium in Contaminated Sediments by Hydroxyapatite Addition, *Environ. Sci. Technol.* 1999, 33, 337-342.
25. McCarthy, J. F., Sanford, W. E., and Stafford, P. L., 1998, Lanthanide Field Tracers Demonstrate Enhanced Transport of Transuranic Radionuclides by Organic Matter, *Environ. Sci. Technol.* 32, 3901-3906.
26. Sowder, A. G., Clark, S. B., Field, R. A. (1999), The Transformation of Uranyl Oxide Hydrates: The Effect of Dehydration on Synthetic Metaschoepite and Its Alteration to Becquerelite, *Environ. Sci. Technol.*, 33(20), 3552-3557.