Apatite II to Remediate Soil or Groundwater Containing Uranium or Plutonium

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Introduction

Uranium (U) and plutonium (Pu) are the two actinide elements most likely to occur as contaminants in the environment. Pu will occur only in a few localized areas associated with weapons production and processing such as Hanford, Rocky Flats and INEEL, and as a result of a very small number of releases from reactor sites such as Sellafield, Kyshtym and Chernobyl. On the other hand, U occurs at most of the same sites as Pu, but also in many other areas as a result of mining operations, machining of depleted-U munitions and natural weathering of igneous rocks and ore bodies which can produce groundwater and surface seeps in the hundreds to thousands of μg/L (ppb) range of dissolved U.

Machining and processing activities (and mining activities for U) produce particulate U and Pu, which can be transported in air as fine material, and physically in soil and water through various physical and biological transport processes. Dissolved U and Pu can be produced by chemical processing, leaching, or weathering of particulates, especially for U. Uranium is transported in groundwater primarily as dissolved U(VI). The dissolved species depends strongly upon the solution pH and dissolved carbonate concentration, as well as other aspects of water chemistry and substrate properties along the transport pathways. In general, UO_2^{2+} dominates in waters less than pH 6, UO_2OH^+ and $(UO_2)_2CO_3(OH)_3^-$ in waters in equilibrium with atmospheric CO_2 between pH 6 and 7, and $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ in most waters above pH 7, and in carbonate-rich waters above pH 6. Pu chemistry is more complex. Depending upon redox and pH conditions, Pu is able to exist in 3 or 4 oxidation states in natural waters, Pu(IV,V,VI) with Pu(III) only stable at low pH under most natural conditions (Runde, 2000). Dissolved Pu is also strongly complexed by carbonate in both the V and VI oxidation states. Generally, Pu exists in oxidized natural waters as Pu(V) in PuO_2^+ and sometimes as Pu(VI) in PuO_2^{2+} (Langmuir, 1997). Pu in most surface soils will depend upon the processing activities at that site that resulted in the contamination and will usually be in several forms having mixed valence states. These states may include the original PuO_{2+x} solids, mixed hydroxycarbonate solids $Pu(OH)_{2x}(CO_3)_y$, true Pu oxyhydroxy-colloids of Pu(IV), Pu-pseudocolloids of SiO_2/hematite/silicate-clays, amorphous solids such as PuO_2OH, and Pu simply sorbed onto mineral particles of various types. A further complexity is introduced by the self-disproportionation of Pu into different valence states, e.g., Pu(V) disproportionates into Pu(IV) and Pu(VI), and Pu(IV) can disproportionate into Pu(III) and Pu(VI). Humic acids facilitate disproportionation making Pu chemistry in soil very dynamic (Langmuir 1997). Alpha-radiolysis of water from radioactive decay can also produce reactive species such as H_2O_2 and radicals that can reduce Pu(VI) to Pu(V), among other reactions.

Therefore, remediation strategies for U,Pu-contaminated soil and groundwater depend heavily upon the environmental conditions, aqueous chemistry and physical setting of the site, and will involve a combination of physical removal and chemical treatment. A combination of sieving, gravity separation, and soil washing can be used to remove the actinide, coupled with simple bulk removal and disposal for extremely hot spots. Pump and treat methods can be used to capture groundwater contamination and above-ground removal methods such as ion exchange or mineralization can be used to strip the water before re-injection or disposal. An *in situ* permeable reactive barrier (PRB) can provide a low-cost alternative to pump-and-treat methods for remediation in groundwater if the hydrology is suitable, or can be used as a barrier to prevent contamination from entering specific downgradient wells, water supplies, surface waters or wetlands that may be at risk. After hot spots have been removed and the general activities are below acceptable levels, either natural processes will act to slowly transport the remaining small amounts of U or Pu offsite or sequester it in phases such as carbonates or natural phosphates over many years. Alternatively, broad site treatments can be applied, such as mixing in soil amendments, establishing wetlands, planting specific vegetation for uptake and stabilization, etc.

Because of the radioactivity associated with U,Pu-contaminated soils and groundwater, special sampling, handling and disposal problems exist in addition to those normally encountered in remediation activities. Evaluating action options will also require specialized testing. Many of these problems and others associated with planning, conducting, evaluating, and documenting radiological surveys for demonstrating compliance with dose or risk-based regulations or standards, are outlined in the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM) or in EPA OSWER 9355.4-16A.

Depleted U is naturally-occurring U that has had most of the more active ^{234,235}U removed, leaving only ^{238}U, with an overall activity of about half that of non-depleted U. The specific activity of depleted U is 360,000 picoCurie per gram (pCi/g). The public dose limit (DCG) for U in drinking water is 35 pCi/L, corresponding to approximately 52 ppb for non-depleted U, or about 97 ppb for depleted U (Abdelouas et al, 1999). Isotopic analysis of U in water and soil can be used to determine the ratio of ^{234,235}U/^{238}U, which can indicate the source of the U as natural (from weathering of igneous rocks and ore bodies) or man-made (from industrial use, manufacturing or handling of depleted U). The public dose limit for Pu in drinking water is 15 pCi/L equivalent to about 0.25 ppb of ^{239}Pu.

Reactive Media – The use of reactive media for remediation of metals and radionuclides is presently being considered for a multitude of field applications. A reactive media can be mixed into soil or waste, or emplaced as a permeable reactive barrier to treat shallow groundwater or surface seeps. A reactive media is any material that has specific chemical reactivities towards one or more chemical constituents via mechanisms such as adsorption, exchange, oxidation-reduction, or precipitation. These materials can have varying ranges of specificity, e.g., adsorption of specific cationic species by a modified zeolite (Sullivan *et al.*, 1994), precipitation of metals and radionuclides by apatite (Fuller *et al.*, 2002; Conca *et al.*, 2000; Bostick *et al.*, 2000), 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).

Materials used for remediation 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. Some of the candidate materials that have been researched include zero valent iron, zeolites, apatites, MgO, carbonates, pecan shells, compost, peat moss, cottonseed meal, and lime. In order to be cost-effective and produced in multiple ton quantities, suitable materials will only be produced by mining operations, agricultural waste production, or industrial waste production, with few modifying steps that must be relatively inexpensive such as cleaning organics off of minerals, crushing old car chases to produce Fe-filings, or coking magnesite to produce MgO.

Numerous studies have been performed for zero valent iron, iron in other forms, polysulfides, granulated activated charcoal (GAC), cottonseed meal and compost (Benner *et al.*, 1999; Blowes *et al.*, 1997; Fruchter, 1996; Tratnyek *et al.*; 1997; Puls *et al.*, 1999; Logan, 2001; Williamson *et al.*, 2000). Results of these studies are well known, and have resulted in many field deployments (Goldstein *et al.*, 2000; Naftz *et al.*, 2000; Hocking *et al.*, 2000; Wickramanayake *et al.*, 2000). However, most of these materials have been successful for solvents and Cr(VI), but have not been generally suitable for most metal contamination in soil, surface waters or shallow groundwaters.

Apatite as a Reactive Media - The apatite mineral group has been shown to be effective both in sequestering dissolved metals and in transforming soil-bound metals to less soluble phases. Utilizing apatite minerals as a remediation method puts to use long-recognized geochemical principles. The groundwork for this research has been laid by previous studies in widely divergent disciplines, including 1) phosphate mineralogy and crystal chemistry (Skinner, 1987, 1989; Skinner and Burnharn, 1968; Wright, 1990a,b; Wright et al., 1990); 2) scavenging and sequestration of minor and trace elements, such as uranium, metals, and the rare earth elements, in natural phosphate deposits (Altschuler et al., 1967; Kovach and Zartman, 1981; Wright et al, 1984; Shaw and Wasserburg, 1985; Keto and Jacobsen, 1987;

McArthur et al, 1990); 3) remediation studies of phosphate/lead systems (Chen et al., 1997a,b; Ruby et al., 1994; Wright et al., 1995; Xu and Schwartz, 1994; Stanforth and Chowdhury, 1994; many papers by Ryan and Zhang, US EPA, especially Zhang et al., 1998; many papers from S. Traina's and T. Logan's groups, especially Ma et al., 1993 and Lower et al., 1998); 4) the impact and accessibility of phosphorus fertilizers to crops (Adepoju et al, 1986); 5) natural analogues in metallic mineral deposits (Koeppenkastrop and DeCarlo, 1988, 1990); 6) phosphate diagenesis during the formation and evolution of phosphorite deposits (McArthur, 1985) and 7) the evidence of changes in the paleochemical evolution of oceans, atmospheres, and climates evidenced by metals, lanthanides, and actinides incorporated into fossil teeth that have an apatite composition (Shaw and Wasserburg, 1985; Keto and Jacobsen, 1987; Wright, 1990a,b).

Apatite minerals form naturally and are stable across a wide range of geologic conditions for hundreds of millions of years (Nriagu, 1974; Wright 1990). Work by Wright, Conca and others (Kovach and Zartman, 1981; Shaw and Wasserburg, 1985; Keto and Jacobsen, 1987; Wright et al., 1987a,b, 1984, and 1990; Conca, 1997) investigated the trace element composition of apatite in fossil teeth and bones and in sedimentary phosphorite deposits through geologic time. They found that sedimentary and biogenic apatite deposited in seawater concentrates metals and radionuclides from the seawater to millions of times the ambient concentration, and locks them into the apatite structure for up to a billion years with no subsequent desorption, leaching or exchange, even in the face of subsequent diagenetic changes in the pore water chemistry, pH, temperatures over 1000° C, and geologic or tectonic disruptions, e.g., uplift, subsidence, erosion and earthquakes. Over 300 apatite minerals exist, with elements from the entire periodic table replacing calcium, phosphate, and hydroxide in the fundamental apatite crystal structure (Deer et al., 1978; Skinner, 1987, 1989). The bioavailability of ingested metal-apatite is also greatly reduced (Davis et al, 1992; Ruby et al, 1992), making animal and human intrusion less dangerous should the metal-apatite phase be ingested, and making bioremediation more effective in mixed waste environments. The reaction between the apatite and metals is rapid (Koeppenkastrop and De Carlo, 1990; Ma et al., 1993; Wright et al., 1995; Chen et al., 1997a,b), and so the treatment is effective immediately, requiring no time for the material to set up. As little as 1% by weight of Apatite II can remediate most metal-contaminated soils (Wright et al., 1995) avoiding volume problems associated with many other methods. For groundwater, a permeable reactive barrier of Apatite II can immobilize over 20% of its weight in metals and can be left in place depending upon the site needs and remediation objectives.

The ultimate driving force for the potentially robust performance of reactive phosphate with respect to metals is the extreme stability of these metal-phosphate phases, some of which are shown in Table 1. The solubilities of quartz and common table salt are also shown for comparison. Common table salt is normally considered very soluble and quartz is normally considered fairly insoluble. Combined with this thermodynamic stability, the rapid kinetics of the metal-phosphate precipitation in the presence of suitable nucleation sites ensures immobilization of the metals, in particular uranium, in the face of most possible transport mechanisms.

TABLE 1. Solubilities of Some Metal-Phosphate Phases*

Mineral Phase	*Product (log K_{sp})*	*Mineral Phase*	*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	$Pu(HPO_4)_2$	-24.4
$Sr_5(PO_4)_3(OH)$	-51.3	UO_2HPO_4	-10.7
$Zn_3(PO_4)_2$	-35.3	Quartz (SiO_2)	-4.0
$Cd_3(PO_4)_2$	-32.6	Salt (NaCl)	0.0

*Nriagu, 1974; Ruby et al., 1994; Geochem, 1994

Apatite as a Reactive Media - The reactive media studied for applications to metal and radionuclide-contaminated sites consists of Apatite II™, an inexpensive, primarily amorphous form of a carbonated hydroxy-apatite that has random nanocrystals of apatite embedded in it, resulting in efficient and rapid precipitation of various phosphate phases of metals and radionuclides, including uranium and plutonium. Apatite II is also an efficient non-specific surface adsorber and is available in multiple-ton quantities at low cost. This material stabilizes metals by chemically binding them into new stable phosphate phases (apatite and autunite minerals) and other relatively insoluble phases in the soil, sediment or in a permeable reactive groundwater barrier. Metals most effectively stabilized by this treatment are lead, uranium, plutonium, zinc, copper, cadmium, nickel, aluminum, barium, cesium, strontium, thorium, cerium, and other lanthanides and actinides.

The mineral apatite is necessary for this technology, especially for instigating heterogeneous nucleation of metal-apatite phases in the undersaturated solutions that make up most contaminated systems (Lower et al, 1998; Conca, 1997; Wright et al, 1995). Non-apatite phosphate and mixtures of precursor constituents will not perform as well, if at all. The apatite works by providing a low but sufficient concentration of PO_4^{3-} in solution (about 100 ppb PO_4^{3-} or less resulting in no phosphate loading or eutrophication, particularly important in ecosystem restoration and maintenance) in order to exceed the solubility of the metal-apatite and result in rapid precipitation of phases such as Pb-pyromorphite or U-autunite, but only in the presence of an existing apatite structure which acts as nucleating site or seed crystal. Apatite is also an excellent material for non-specific adsorption of most cationic metals from solution. Apatite is an excellent buffer for neutralizing acidity through PO_4^{3-}, OH^-, and substituted CO_3^{2-}, exerting control over chemical activities of other species leading to the precipitation of oxihydroxide- and carbonate-metal phases. Apatite II will sequester up to 20% of its weight in metals, particularly Pb and U, even in the presence of high ionic strength solutions such as percent levels of nitrate. Apatite II will buffer most waters to pH 6.5 to 7, particularly acid rock drainage and wastewater from chemical processing.

Knowledge of the metal sorption mechanism is critical for evaluating the effectiveness of apatite or any reactive media for immobilizing that contaminant in remediation applications. For example, adsorption of U(VI) on the apatite surface would result in a lower PRB holding capacity for U(VI) removal than a precipitation process because adsorption can sequester only a few percent of U by weight of the material, whereas precipitation can remove an order of magnitude more by forming completely new solids made mostly of U by weight. The relative contribution of adsorption and precipitation to metal removal depends upon the environmental conditions, the mineral phases present, and the metal concentration in solution. Simple feasibility studies on the contaminated groundwater and soil under site conditions would determine which mechanism would dominate at any particular site. In soil column feasibility studies investigating the use of Apatite II in remediating U from groundwater at Oak Ridge, the predominant mechanism was precipitation of autunite onto the Apatite II surfaces (Bostick et al., 2000).

The nominal composition of Apatite II is $Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$ where $x < 1$. For U removal via precipitation, the overall reaction is actually a dissolution reaction of the Apatite II followed by precipitation of autunite, $Ca(UO_2)_2(PO_4)_2 \bullet 10H_2O$, on existing Apatite II surfaces, simplified as:

$$\underset{\text{Apatite II}}{Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2} + 14H^+ \rightarrow (10-x)Ca^{2+} + xNa^+ + (6-x)[H_2(PO_4)]^- + xH_2CO_3 + 2H_2O \qquad (1)$$

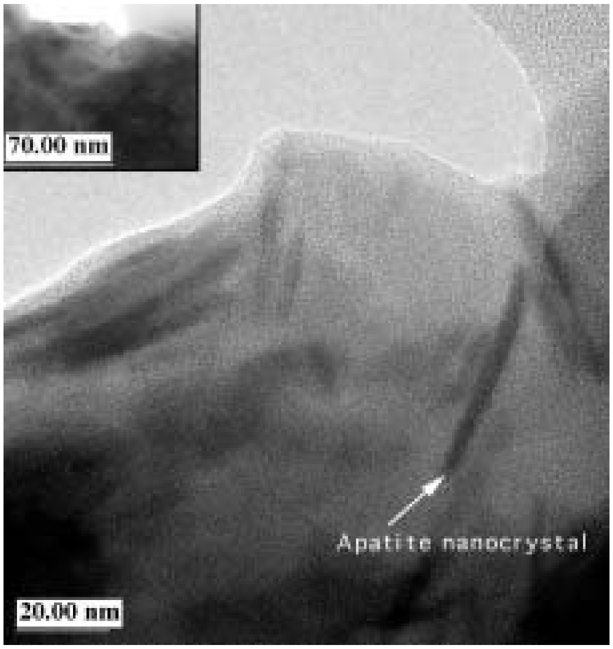
$$2UO_2^{2+} + Ca^{2+} + 2H_2(PO_4)^- + 10H_2O \rightarrow \underset{\text{autunite}}{Ca(UO_2)_2(PO_4)_2 \bullet 10H_2O} + 4H^+ \qquad (2)$$

Similar reactions occur for Pu-phosphate. The degree of protonation of the phosphate and carbonate, and the exact actinide species involved, depend upon the pH and aqueous chemistry. The above example is for the range of pH between 3 and 6 in Oak Ridge groundwater in equilibrium with air. Reaction (1) does not usually lead to reaction (2), but provides a constant supply of phosphate to solution to induce reaction (2) whenever UO_2^{2+} is in solutions contacting the apatite. This excess dissolution leads to the strong pH buffering exhibited by Apatite II from reaction (1). Autunite can subsequently dehydrate in air to meta-autunite $Ca(UO_2)_2(PO_4)_2 \bullet 6.5H_2O$ as was seen in Apatite II column studies at Oak Ridge (Bostick et al., 2000) and can further dehydrate to even lower hydration states under dry soil conditions. Chernokovite, or hydrogen-autunite, $H_2(UO_2)_2(PO_4)_2 \bullet 10H_2O$, can also form in reactions with apatites, as was seen in column studies with Apatite II and 1 ppm U in distilled water with a much lower dissolved calcium concentrations (Leah Matheson, personal communication), and in batch studies with reagent hydroxyapatite and various U concentrations in distilled water and groundwater (Fuller et al., 2002).

The solubility of the newly-formed phase controls the equilibrium concentration of U or Pu in solution. Therefore, equilibrium concentrations are usually reduced to below regulatory limits, if not detection limits, because of the extremely low solubilities of metal-phosphate phases, e.g., $K_{sp} = 10^{-49}$ for autunite and $K_{sp} = 10^{-24}$ for $Pu(HPO_4)_2$. Differences in the performance among various apatite phases result mainly from differences in those properties that influence the kinetics and solubility, e.g., crystallinity (a higher degree of crystallinity decreases solubility and dissolution rate, making the apatite less reactive), and minor element chemistry (presence of carbonate decreases lattice stability, increasing solubility and dissolution rate; presence of F increases lattice stability, decreasing solubility and dissolution rate).

Apatite Sources - There are several apatite sources with widely varying reactivities and properties, and not all are appropriate for metal remediation. For metal remediation, the apatite should: 1) be fully carbonated with as much carbonate ion substituted as possible; 2) have no fluorine substitution in the hydroxyl position; 3) have few trace metals initially in the structure; 4) be poorly crystalline or amorphous, but have sufficient nucleation sites for metal-phosphate precipitation and 5) have a high internal porosity (Conca, 1997). These characteristics either increase the reactivity of the material (which is still extremely low) or increase its metals-holding capacity. For these reasons, traditional phosphate ores and cow bone, charred or not, are not optimal (Bostick et al., 2000). Apatite II exhibits all of these properties. Figure 1 is a High-Resolution Transmission Electron Microscopy image (HR-TEM; Lu et al., 2001) showing the structural properties of the Apatite II. All other apatites are much more crystalline and less effective for remediation of metals.

Figure 1. HR-TEM image of Apatite II showing the general amorphous nature of the matrix with random nanocrystal inclusions of crystalline apatite embedded throughout.



Results from Previous Studies

Uranium - Various reactive materials were tested for the removal of dissolved uranium (U) from DOE Y-12 facility NT–1 groundwater at Oak Ridge, Tennessee (Bostick et al., 2000) including Apatite II, charred cow bone, zeolites, mixed valent oxide iron filings and metal, granular activated charcoal (GAC), phosphate rock (apatite ore), peat moss, Dowex resin, Nucon Nusorb, and Mersorb-3. The difficulty at this site is that the groundwater can have high total dissolved solids, especially nitrate ion, and contains elevated levels of many regulated metals including U, Cd, and Pb. Apatite II was shown to be almost ten times as effective as bone char for removing U, and many orders of magnitude more effective than the other materials, even in the presence of high nitrate concentrations. Some of the results are shown in Figure 2. In sorption experiments, K_d is the distribution coefficient for the element of interest and is the ratio of the amount of the element on the solid compared to the amount in solution. The larger the value of K_d the greater the ability of the material to remove the element from solution. X-ray diffraction (XRD) showed meta-autunite crystallized on the surfaces of the Apatite II.

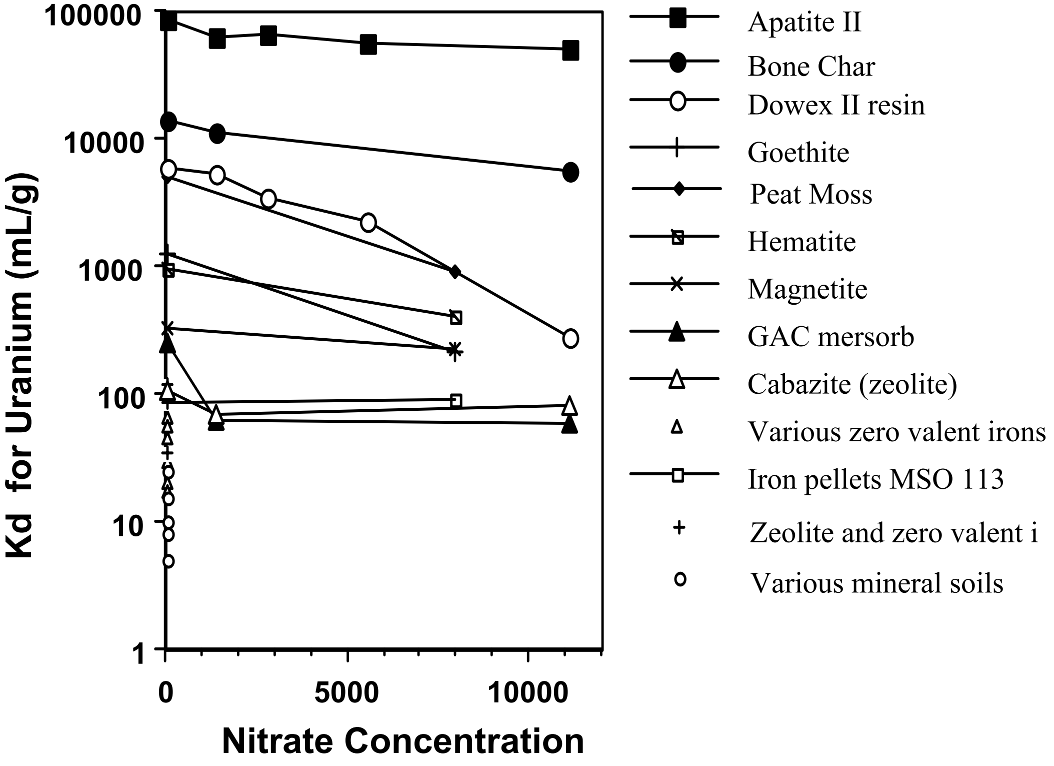


Figure 2. Sorption results for various reactive media in U–contaminated groundwaters from Oak Ridge. Apatite II performed better than all other materials, even under high nitrate concentrations (from Bostick et al., 2000).

Further studies with Apatite II at this site used column studies with U-contaminated groundwater infiltrating Apatite II columns bounded on either side by inert denstone sand (Figure 3). Influent uranyl nitrate waters with ppm levels of uranium flowed through the columns for several months. No uranium above 3 ppb exited the Apatite II in any columns. The loading of uranium near the influent end of the column array was high (up to 2.4 wt% U in the samples examined). Analysis of the material near the influent end showed Apatite II coated with U-bearing phases (Figure 4) identified as hydrogen autunite (chernikovite) in XRD. This material was subjected to a TCLP test (EPA Method 1311) and the leachate contained 0.315 µg-U/L (or 0.315 ppb U), which is well below the permissible

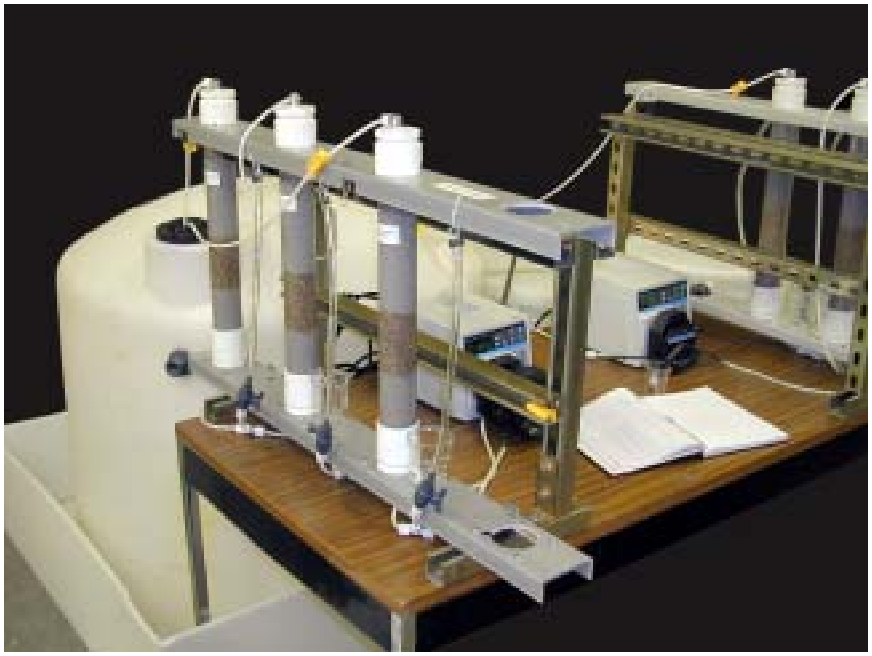


Figure 3. Column Studies for Apatite II Permeable Reactive Barrier at Oak Ridge Y-12 site. The Y-12 groundwater influent is contaminated with ppm levels of uranium (from MCLInc., and MSE, Inc.).

Figure 4. SEM-EDS photomicrograph of a uranium-rich grain on Apatite II from one of the columns. The plate-like structure is typical of the autunite mineral group and spectra indicate autunite (from MCLInc.).

drinking water standard of 35 pCi/L. The percentage of total U from the sample that was mobilized by the extraction procedure was less than 0.0003%.

Apatite II was also tested as part of a Containerized Vat Leaching process (CVT) at a depleted-uranium firing range at Los Alamos. Soil contaminated with U, was leached with bicarbonate solution to remove the U. The U was then removed from solution using Apatite II instead of exchange resins. Soil, mixed with a small amount of Na_2O_2 to oxidize any reduced U to U(VI), is heaped into containers, then infiltrated from below with bicarbonate solution that goes into a settling-acidification basin and then into sorbent canisters filled with Apatite II. The cleaned soil is sampled, placed back on the ground, or used for other purposes, and the concentrated U-product is disposed of as low-level waste. Figure 5 shows the U concentration going from the effluent exiting the leaching step (37 ppm U) to the effluent exiting the Apatite II (less than 0.01 ppm). The volume reduction in contaminated materials is on the order of 1000 times. TEM images of the Apatite II after treatment showed newly-precipitated U-bearing phases covering all available surfaces of the Apatite II (Figure 6). Phase identification was not possible for this sample, but similar samples showed autunite precipitation.

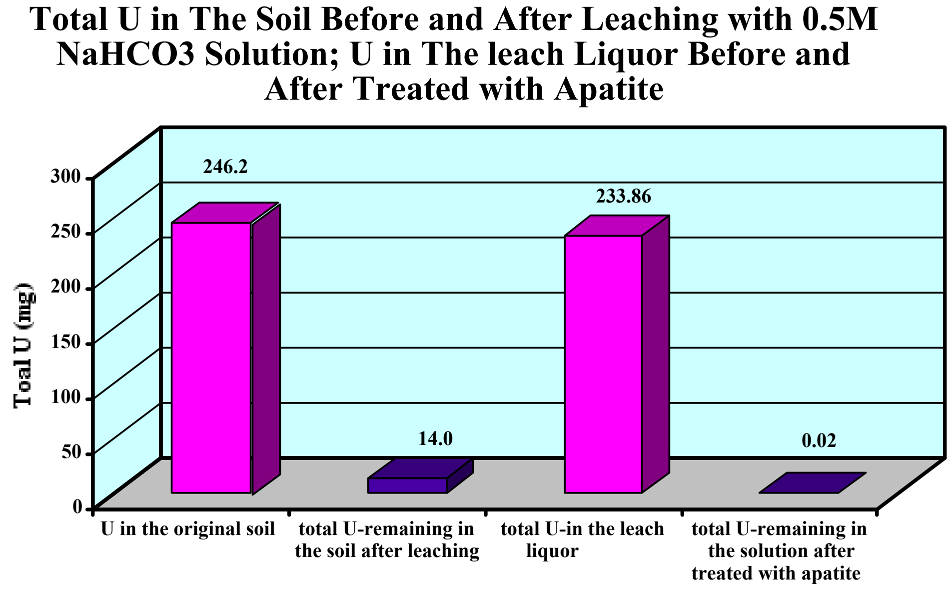


Figure 5. Performance of CVT in Treatability Study. Original soil refers to soil before any treatment. After leaching result refer to soil after leaching with bicarbonate solution. Total U in leach liquor refers to bicarbonate solution exiting the soil. After treatment with apatite refers to solution after leaving the Apatite II.

Plutonium - 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 permeable reactive barrier consisting of Apatite II as the primary reactive agent (Conca et al., 2002; Taylor et al, 2002). Nitrate, perchlorate, Pu, Am, and ^{90}Sr concentrations were reduced to below their maximum concentration limits (MCL) and usually to below detection limits in these laboratory studies. Figure 7 shows the Pu sorption batch results for various materials and combinations. Am and Sr batch tests were also run. 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

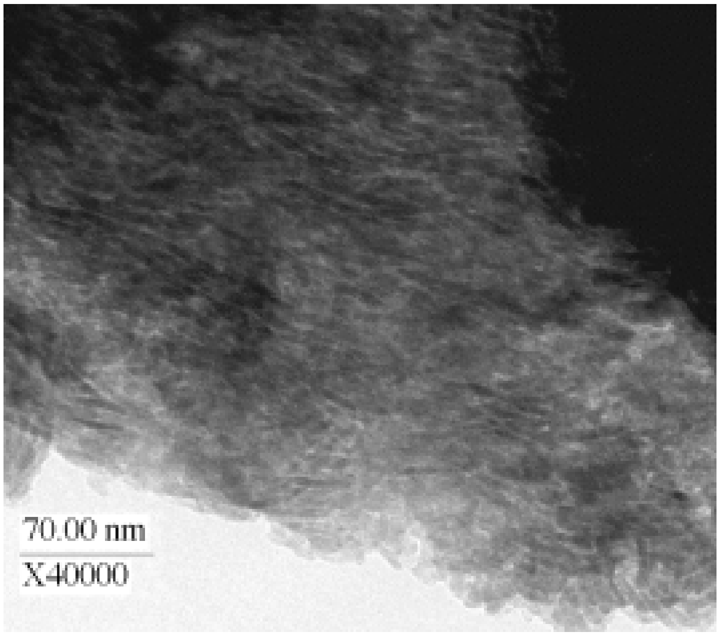


Figure 6. HR-TEM image of Apatite II after treatment of leachate from uranium-contaminated soil during the soil washing operation. Uranium is completely covering the surface of the Apatite II. Phase identification was not done on this sample, but in similar experiments, the phase was identified as autunite.

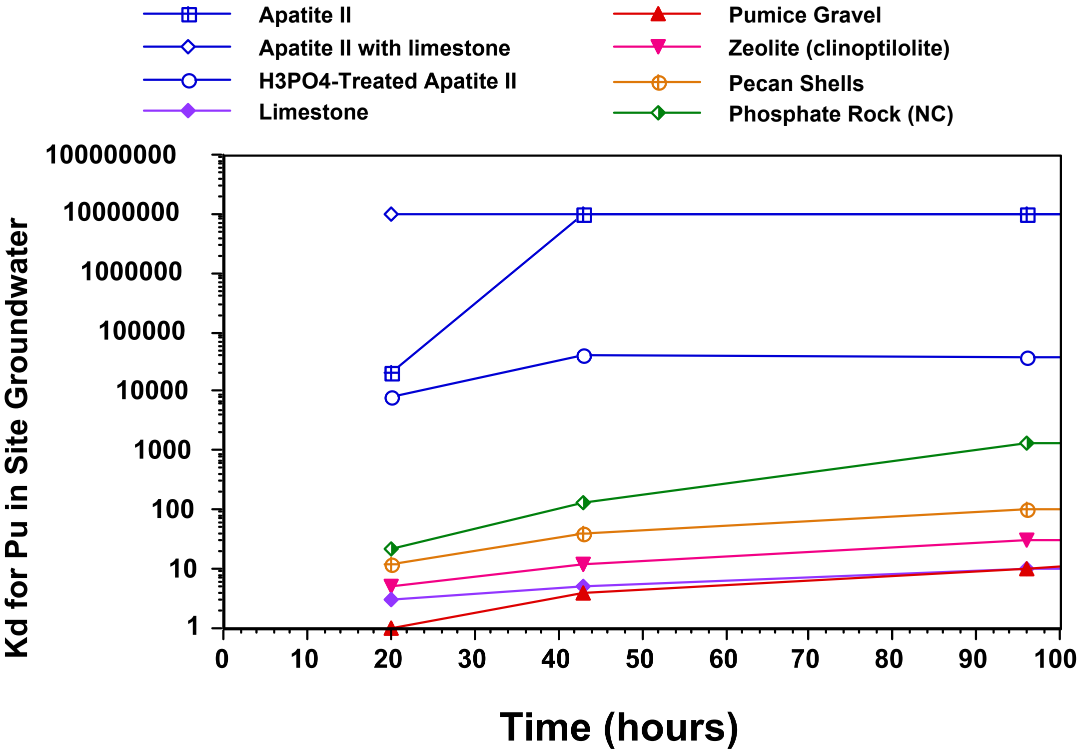


Figure 7. Sorption batch tests of Pu for various materials for the Mortandad Canyon barrier.

and Wright, 1995; Bostick *et al.,* 1999; Runde, 2000). For plutonium, the various samples of Apatite II exhibited the highest K_d values, approaching 10,000,000. The mineral apatite (phosphate rock) exhibited notably poorer performance. For americium (not shown), 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 respect to Sr, with K_d values of about 500, all K_d values were less than 1,000. 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 reduced values in the laboratory batch tests may reflect kinetic effects.

A column test was also run with Apatite II using spiked groundwater from the site. A 100 mL pulse of well water spiked with 7 x 10^{-9} M ^{85}Sr, 5 x 10^{-7} M ^{239}Pu (750,000 pCi) and 1 x 10^{-9} M ^{241}Am was injected into the column after a two-week equilibration period. These radionuclide concentrations represent about 60 years of flow at present plutonium concentrations at the site, 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. Analysis of column elutants was conducted for three months until the experiment was interrupted by the Cerro Grande fire. After injection of the contaminant pulse, approximately 300 pore volumes exited the columns with no detectable nitrate, perchlorate, Pu, Am, or Sr in the effluent. The immobilized Pu, Am, and Sr, therefore, appear stable against future subsequent flow, at least for this number of pore volumes, a condition that should be addressed if the spent barrier materials need to be left in place after the plume is treated. Separate columns of Apatite II were run with nitrate at high levels (250 mg/L) and perchlorate at field concentrations (0.4 mg/L). The Apatite II removed both constituents to below detection as a result of the residual organics on the Apatite II supporting a robust denitrifying microbial population, an unanticipated advantage to the Apatite II.

Apatite was also investigated as a possible backfill component at the Waste Isolation Pilot Plant (WIPP) in Carlsbad, NM, to prevent Pu(VI) migration from transuranic waste (Conca et al., 2000). Experiments

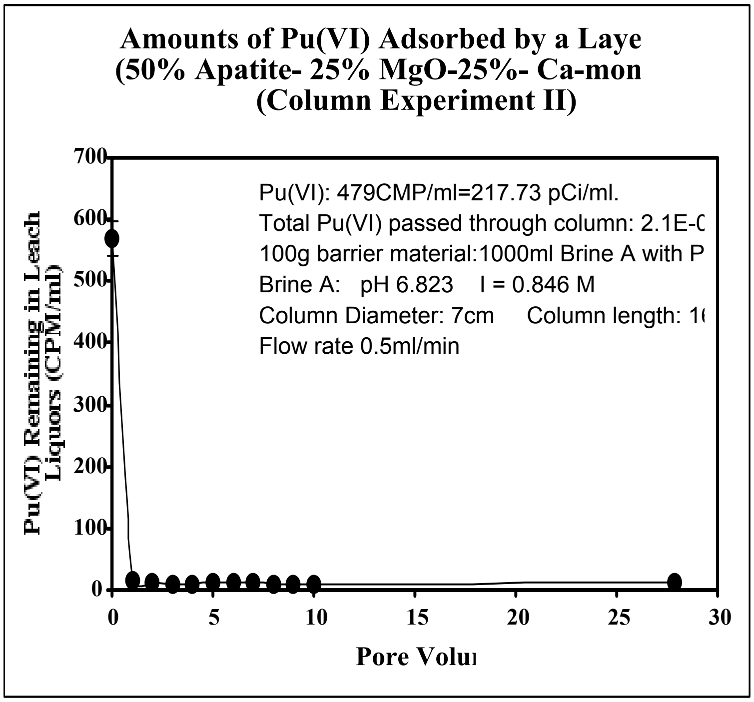


Figure 8. Pu(VI) retardation by a layered Apatite/MgO/Montmorillonite engineered barrier.

using Pu(VI) in WIPP Brine A infiltrating through various backfill combinations showed adding an Apatite layer to MgO/montmorillonite increased performance substantially, and that layering performed much better than mixing the materials together. Placing the apatite as the first layer increased performance over 100 fold. Figure 8 shows results from one of the layered backfill column experiments with a 50%Apatite/25%MgO/25%montmorillonite barrier. The initial infiltration concentration of 570 CPM/ml dropped to 10 CPM/ml after the brine moved through the barrier.

Conclusions

Apatite II is a reactive media that appears well-suited for the remediation of metal-contaminated soils and groundwater, including uranium and plutonium. It exhibits large sorption coefficients (K_d values of almost 100,000 for U and over 1,000,000 for Pu) and can be loaded fairly heavily, e.g., percent levels, although other work indicates up to 20% by weight of the Apatite II (Conca, 1997). Field remediations have performed with Apatite II for Pb, Cd and Zn in contaminated groundwater at acid mine sites and soil in a military munitions site. These field implementations provide realistic field emplacement costs for both soil mixing and permeable reactive barrier emplacement (Calabretta et al., 2001; see also www.pimsnw.com). The soil mixing of 5% Apatite II by weight of soil to treat particulate Pb totaled only $23 per treated ton of soil. The PRB emplacement is treating every 1,000,000 gallons of water contaminated with Pb, Cd and Zn for a cost of $40 of Apatite II. These figures use the existing production costs of $500/ton of Apatite II. While very cost-effective relative to other treatment methods, these costs could be further reduced by three to four times using new production methods. These costs will be similar for those associated with U and Pu, e.g., about $25/treated ton of contaminated soil and about $50 per treated 1,000,000 gallons of water at U/Pu concentrations of 1 ppm. These costs do not include those necessary for handling radiological materials, radiological site characterization and other DOE site issues, costs which will be incurred regardless of the technology used and do not effect the actual emplacement costs of Apatite II.

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