PIMS USING APATITE II™: HOW IT WORKS TO REMEDIATE SOIL & WATER

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ABSTRACT: Phosphate-Induced Metal Stabilization (PIMS™) using Apatite II™ stabilizes a wide range of metals, especially Pb, U, Cd, Zn, Cu and Al, *in situ* or *ex situ*, by chemically binding them into new phosphate minerals and other low-solubility phases that are stable over geologic time. The excellent stabilization efficiency comes from the extremely low solubility products (K_{sp}) of the resultant metal-apatites, e.g., for Pb–apatite (pyromorphite) $K_{sp} \sim 10^{-80}$ (Nriagu, 1984; Ruby *et al.*, 1994) to $K_{sp} \sim 10^{-167}$ (Manecki *et al.*, 2000). Combined with this thermodynamic stability, the rapid kinetics of the metal-phosphate precipitation and adsorption ensures immobilization of metals in the face of most transport mechanisms. Depending upon the metal, the concentration of the metal and the aqueous chemistry of the system, Apatite II works by four general, non-mutually-exclusive processes. This technology has been successful with contaminated range soils, groundwaters and wastewaters for Pb, U, Cd, Zn, Al and Cu, and has stabilized between 5% and 50% of its weight in metals depending upon the metal and the environmental conditions. Costs for range soil remediation are \$20-\$30/yd^3 (see accompanying paper in this volume, Wright *et al.*, 2004) and costs for water remediation are \$40 per 1,000,000 gallons of water per mg/L of metal.
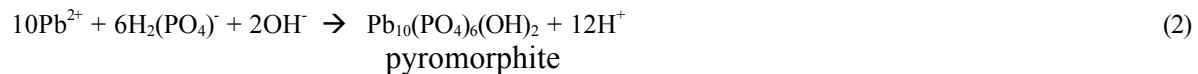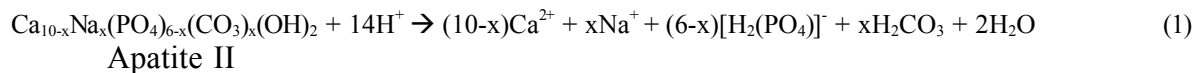
INTRODUCTION

Apatite II has the suitable characteristics of substituted CO_3^{2-}, no substituted F, low trace metal concentrations, poor crystallinity (>90% amorphous; Conca *et al.*, 2000), and high microporosity necessary for optimal performance in the field that other apatites do not have (Lu et al., 2001). Apatite II [$Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$ where x < 1], has been developed from fish bones (U.S. Patent #6,217,775) as the most reactive, most cost-effective apatite or phosphate available. Additionally, Apatite II is generated as a waste product from the commercial fish industry, but is used as a remediation product and, thus does not contribute to environmental cost, further enhancing the advantages of the PIMS with Apatite II technology over other apatite or phosphate technologies. This is in part because agricultural grade or reagent grade phosphates and phosphoric acid or mineral apatite require production from phosphorite deposits and, as such, create excessive waste and environmental hazards through their generation and contribute to long term environmental costs. As an example, central Florida is experiencing an environmental crisis stemming from phosphoric acid and phosphate production from open pit mining of mineral apatite in phosphorite deposits (see http://www.fipr.state.fl.us/publication, 2003). Planned phosphorite mining activities also threaten the last habitat of the remaining Florida panthers and will cause extinction of the species, an effect that must be factored into costs for any technology (http:// www.nwf.org/panther, 2003). There are no environmental impacts from using or producing Apatite II. Apatite II can be mixed in with contaminated soil or waste, can be emplaced as a down-gradient permeable reactive barrier, or can be used as a liner. There is no phosphate loading to the environment when using Apatite II because of its already low solubility, $K_{sp} < 10^{-20}$.

HOW APATITE II WORKS

Apatite II works to sequester metals by four general, non-mutually-exclusive processes depending upon the metal, the concentration of the metal and the aqueous chemistry of the system. In the first process, Apatite II continuously supplies a small, but sufficient, amount of phosphate to solution to exceed the solubility limits of various metal-phosphate phases such as pyromorphite and autunite (Manecki *et al.*, 2000). Under almost any environmental condition conceivable, Pb-pyromorphite will precipitate only by heterogeneous nucleation, i.e., a seed crystal with the apatite crystal structure is necessary for precipitation to occur. Homogeneous nucleation (precipitation directly from solution without a seed crystal) will not occur unless Pb concentrations exceed about 10 ppm (Lower et al, 1998a, 1998b), a condition rarely achieved in the environment, even for acid mine drainage. This observation is absolutely critical for successful phosphate technologies, which are more appropriately named apatite technologies because apatite is required for the long-term stability of Pb by precipitation of pyromorphite. Without apatite, other Pb-phases will form that have much higher solubilities (Nriagu and Moore, 1984). The Apatite II grains serve as an optimal seed crystal as well as an optimal source of phosphate. Therefore, with the use of Apatite II, over the course of time all migrating Pb in the system precipitates as Pb-pyromorphite. These microscopic Pb-pyromorphite mineral phases will grow and coalesce as a result of the process of Ostwald ripening (Morse and Casey, 1988) eventually forming larger mineral clusters. During this process, which can take many years, the concentration of Pb in solution is kept extremely low, <15 ppb, by the presence of the Apatite II-supplied phosphate, so that no leaching of Pb occurs above drinking water limits, the material is no longer hazardous according to TCLP tests and field leachate monitoring and bioavailability is reduced.

The reaction between the apatite and metals is very rapid (Koeppenkastrop and De Carlo, 1990; Ma *et al.*, 1995; Wright *et al.*, 1995; Chen *et al.*, 1997a,b, Manecki *et al.*, 2000), and so the treatment is effective immediately. Although the reaction is rapid on the molecular scale, the macroscopic flow parameters (grain size, flow rate, barrier design) are the limiting factors in the field insofar as they determine the efficiency with which dissolved metals come into contact with the surfaces of the reactive media. For Pb, the reaction is actually two-steps, a dissolution reaction followed by a precipitation reaction:

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

Apatite II

$$10Pb^{2+} + 6H_2(PO_4)^- + 2OH^- \rightarrow Pb_{10}(PO_4)_6(OH)_2 + 12H^+ \qquad (2)$$

pyromorphite

The degree of protonation (the number of hydrogen ions attached to the PO_4^{3-}) in the intermediate reactions depends upon the pH. The above example is for the range of acid soils or acid mine drainage, pH < 6. Reaction (1) does not necessarily lead to reaction (2). However, whenever Pb^{2+} is in solution in contact with the apatite, the apatite provides a constant supply of phosphate to the solution to induce reaction (2). This excess dissolution leads to the strong pH buffering exhibited by Apatite II as a result of reaction (1). The solubility of the original apatite is key to the effectiveness of this mechanism; it must be sufficiently high to be reactive, but sufficiently low to persist in the environment for many years and to prevent phosphate loading. In closed systems (batch tests) the rate of dissolution of the apatite is strongly affected

by the contaminant concentration because the system approaches equilibrium. On the other hand, in open systems (PRBs, soils or soil columns) the rate of dissolution of the apatite is little affected by the contaminant concentration since the system rarely approaches equilibrium because dissolved constituents are rapidly removed from the system either by flushing or sorption (precipitation or adsorption).

In the second process, Apatite II acts as an excellent buffer (buffers to pH 6.5 to 7) for neutralizing acidity through its PO_4^{3-}, OH^-, and substituted CO_3^{2-} groups, and buffering to neutral pH alone is effective at precipitating many metal phases, particularly Al and Fe (Conca *et al.,* 2000).

The third process is surface chemi-adsorption. Apatite II is the best material available for non-specific metal adsorption, particularly of the transition metals, through its uncompensated phosphate and hydroxyl surface groups. Apatite II will adsorb up to 5% of its weight by this process (Ma *et al.,* 1995; Manecki *et al.,* 2000; Conca *et al.,* 2000).

The fourth process is biological stimulation. Over many years, Apatite II supplies both P and readily-bioavailable organics at low but optimal concentrations for stimulating microbial communities. As an example, in the presence of sulfate and Apatite II, Zn and Cd are reduced to sulfides, even in waters that originate as highly oxidizing (acid mine drainage and wastewater).

The bioavailability of ingested metal-apatite is also greatly reduced (Ruby *et al.*, 1994). This makes animal and human intrusion less dangerous if the metal-apatite phase is ingested. The presence of Apatite II makes bioremediation and phytoremediation more effective in mixed waste environments by reducing metal toxicity to microbial and plant communities.

Similar reactions occur for U, Ce, Pu and other metals for which precipitation is the primary process of removal from solution. The solubility of the new phase controls the concentration of the metal in solution. Therefore, metal concentrations are usually reduced to below regulatory limits, if not detection limits, because of the extremely low solubilities of metal-phosphate phases. Differences in the performance among various apatite phases result from differences in those properties that influence the kinetics and solubility, e.g., crystallinity and minor element chemistry. A higher degree of crystallinity decreases solubility and dissolution rate, making the apatite less reactive and less effective, whereas lower crystallinity increases solubility. Thus, the amorphous form of the solid is the most reactive. The presence of F as a minor constituent in the apatite structure increases lattice stability, decreasing solubility and dissolution rate. The presence of carbonate as a minor constituent in the apatite structure decreases lattice stability, increasing solubility and dissolution rate.

However, for Zn, Cd and other transition metals, adsorption or precipitation into non-apatite phases are the primary mechanisms under most environmental conditions. Therefore, the performance with respect to these metals, and their solution concentrations, depends upon the adsorption characteristics of the apatite and properties such as the amount and type of organics, solution chemistry, surface properties, grain size, degree of crystallinity, and competing ions. Just as adsorption characteristics of amorphous silica are much greater than quartz, the adsorption characteristics of the primarily amorphous Apatite II are much greater than other apatites. Metal concentrations in waters treated with Apatite II will usually be below regulatory limits for Zn and Cd, if not detection limits, because of the strong chemi-adsorption properties of the Apatite II.

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 minimal 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. Apatite II exhibits all of these properties while phosphate rock (mineral apatite) and cowbone (charred or uncharred) do not (Lu *et al.*, 2001). The cow bone is a less effective phosphate material for remediation of metals because of its higher crystallinity. The apatite in all phosphate rock is also less effective because of its high crystallinity, the large amount of F substitution, the lack of carbonate substitution, the low internal porosity and the high trace metal content.

APPLICATIONS

Comparisons of different apatite materials under various conditions and for various metals demonstrates how these properties influence performance. Figure 1 shows traditional desorption batch leach test results from untreated soil and soil treated with different apatites. Apatite II was the only apatite able to reduce metal concentrations to below the EPA Maximum Concentration Limit (MCL) at all amendment amounts, and reagent grade hydroxyapatite is a close second. In various column experiments, Apatite II immobilized over 17% of its weight in Pb, precipitated as pyromorphite.
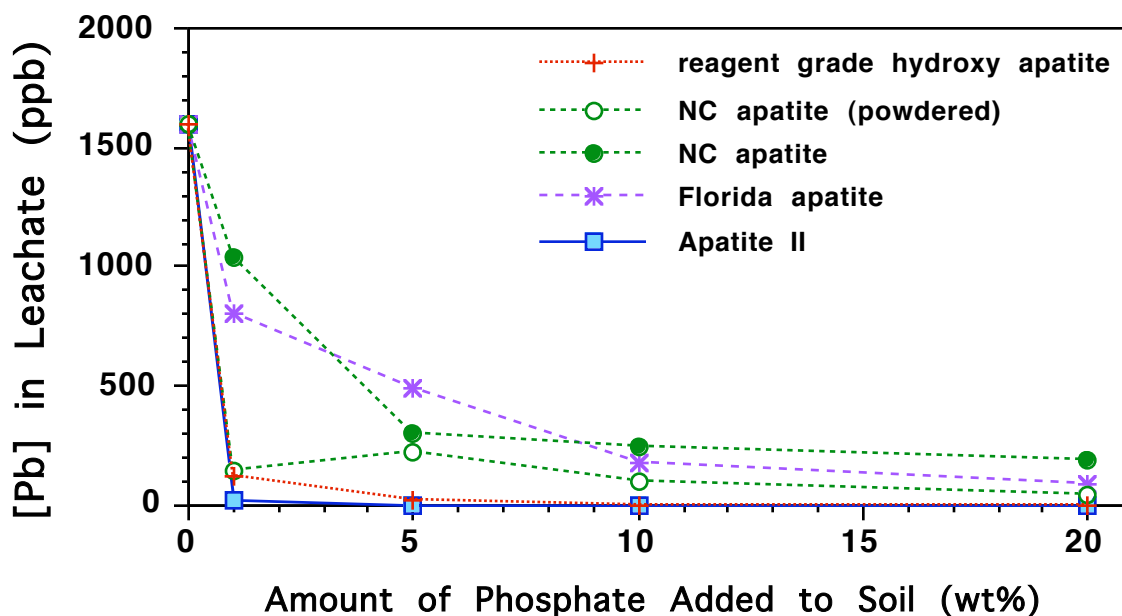

Figure 1. Pb isotherms determined from batch tests showing concentration of Pb in leachate from soil contaminated with 4170 ppm Pb after amendment with various amounts of phosphate rock, reagent grade apatite and Apatite II.

Various reactive materials were tested for the removal of dissolved uranium (U) from DOE Y-12 facility NT−1 groundwater at Oak Ridge, TN including Apatite II and bone char. The groundwater at this site can have high total dissolved solids, especially nitrate ion, and can contain elevated levels of many regulated metals including U, Cd, and Pb (Matheson *et al.*, 2002). Apatite II, with distribution coefficients (K_d) of about 100,000, was shown to be almost ten times as effective as bone char for removing U, and many orders of magnitude more effective than

all other materials, even in the presence of high nitrate concentrations, up to 11,000 ppm nitrate (Conca *et al.*, 2000). X-ray diffraction showed meta-autunite crystallized on the surfaces of the Apatite II. In separate column experiments Apatite II immobilized up to 50% of its weight in U (Matheson *et al.*, 2002), precipitated as chernikovite (Figure 2).

Figure 2. SEM photomicrograph of a uranium-rich grain precipitated on Apatite II from the column experiments. The plate-like structure is typical of the autunite mineral group and XRD indicated chernikovite (from Matheson *et al.*, 2002).

Apatite II has been used to remediate various types of firing range soils at several sites (see associated paper in this volume, *PIMS using Apatite II: Remediation of Pb-Contaminated Range Soil at Camp Stanley Storage Activity, TX*, Wright *et al.*). At Camp Stanley in Boerne, Texas, Apatite II was used to remediate 3,000 yd^3 of Pb-contaminated soil by *in situ* soil mixing. The Apatite II treatment reduced the average leaching of Pb from 0.373 mg/L in untreated soil to 0.003 mg/L in treated soil, as observed from lysimeter wells, eliminating potential impacts to groundwater and surface water run-off. Waste classification results from Toxicity Characteristic Leaching Procedure (TCLP) tests gave an average of 0.46 mg/L Pb for treated soils meeting the State of Texas class 2 non-hazardous waste classification criteria of 1.5 mg/L Pb, which made the treated soil non-hazardous, while the untreated soil did not meet these criteria. Apatite II treatment also reduced the Pb bioaccessibility of the soil. Studies with soluble phosphates on other range soils showed that the soluble phosphates actually caused greater Pb and phosphate migration both vertically through the soil and horizontally in the suspended load during runoff. However, with Apatite II vertical Pb migration was reduced to below 8 ppb in solution. Apatite

II stabilization did not allow transport of Pb in runoff because precipitated Pb-pyromorphite as well as small Pb particles adhere to the silt and sand-sized Apatite II (Figure 3).
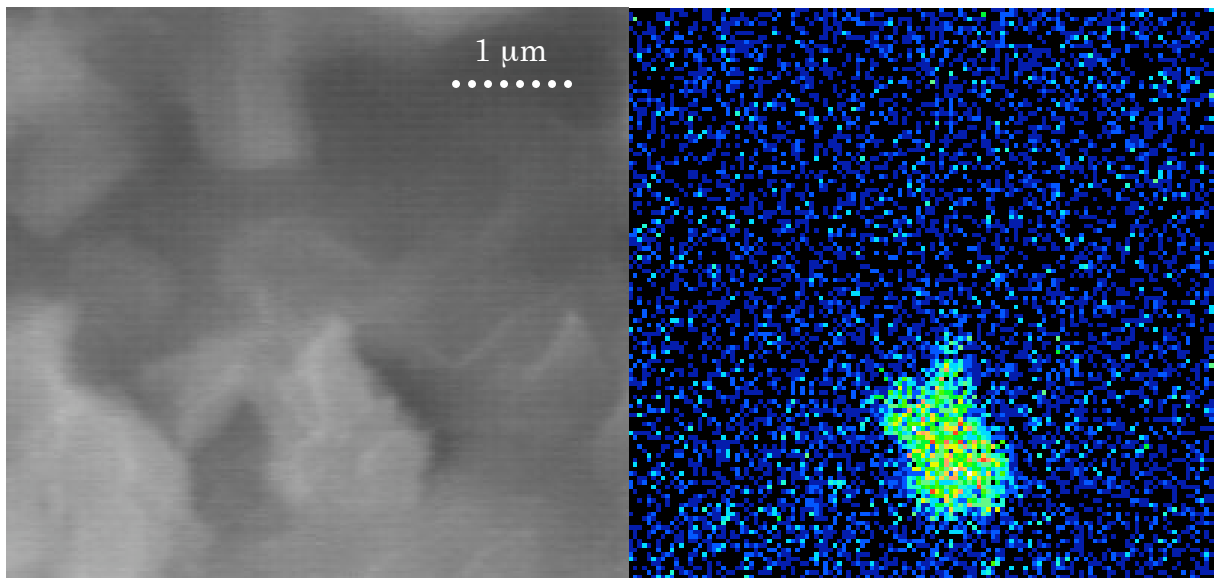

Figure 3. Left: SEM photomicrograph showing a 1-micron wide Pb grain adhered to an Apatite II surface in treated soils from Camp Stanley. Right: Pb X-ray map.

An example of all four processes working together (precipitation, pH buffering, chemisorption and biological reduction) is at the Success Mine and Mill site in northern Idaho, where PIMS using Apatite II is being used in a subsurface permeable reactive barrier to treat shallow alluvial groundwater containing elevated levels of zinc, lead, cadmium, sulfate and nitrate. Based upon laboratory feasibility studies of nine reactive media, Apatite II was selected for use as a PRB in a voluntary non-time critical CERCLA removal action. The impacted groundwater is treated *in situ* before it enters the East Fork of Ninemile Creek, a tributary to the Coeur d'Alene River. The emplaced Apatite II PRB has been operating successfully since January of 2001, reducing the concentrations of Pb and Cd from ppm levels to below detection (2 µg/L), Zn from over 100 ppm to near background (about 100 µg/L) and sulfate and nitrate from over 200 ppm to below detection (50 µg/L). The PRB has sequestered over 100 lbs of Cd, over 200 lbs of Pb and over 9,000 lbs of Zn over the 3 years since it was emplaced, and less than half of the Apatite II in the PRB has been spent.

The Apatite II has acted as an ideal substrate and nutrient source for microbial communities in this PRB. Table 1 shows typical analyses for dissolved constituents entering and exiting the barrier. Comparison of the influent and effluent pH, sulfate, nitrate, ammonia, phosphate, and bicarbonate concentrations, shows that Zn is being incorporated into sulfide phases through precipitation. XRD and SEM analyses indicate that the precipitated grains are a mixture of sphalerite and recrystallized apatite. Portable probes were used to measure pH, Eh (oxidation/reduction potential), dissolved oxygen (DO), temperature, and conductivity at various points within the system (Neal Yancy, INEEL, personal communication). Oxygen probes gave DO concentrations of between 0.1 and 0.3 mg/L within the barrier, and over 4.0 outside the barrier. Eh values within the first cell of the barrier were over +550, while most of the barrier interior was between –100 and –300. Pb and Cd disappear completely from solution within the

first few feet of the barrier, and Zn concentrations decrease continuously throughout the barrier, finally dropping to about 0.1 mg/L or below before exiting the barrier. *Entercocci* was found to be the only microbe in significant amounts within the barrier, measured at 16,000 MPN/100ml at the outflow, where MPN represents the most probable number. This number decreases rapidly to below the recreational guideline for *Entercocci* in fresh water (30 MPM/100ml) once the outflow leaves the area of the PRB. There was no P-loading above the background range observed in other drainages downstream (between 2 and 20 mg/L total dissolved phosphorous).

Investigation of materials collected from the barrier, and geochemical modeling using MINTEQ and PHREEQ were performed in order to determine which mechanisms are operating in the field and how long the barrier should last. MINTEQ results using the compositions in Table 1 indicate pyromorphite and sphalerite (ZnS) are the most stable phases within the barrier for Pb and Zn. Modeling is uncertain with regard to Cd, which could be both adsorbing onto the Apatite II and precipitating as a sulfide similar to Zn.

Table 1. Changes in Some Groundwater Constituents Entering/Exiting the Apatite II PRB

Species	Entering Barrier (mg/L;ppm)	Exiting Barrier (mg/L;ppm)
pH	4.18	7.13
Al	3.16	0.020
As	0.0007	0.0004
Ca	26.0	44.5
Cd	0.42	<0.001
Cl	0.45	1.05
Co	0.0069	<0.001
Cr	<0.001	<0.001
Cu	0.23	0.0014
F	0.24	<0.02
Fe	0.05	0.11
HCO_3	<0.001	297.0
K	1.27	1.54
Mg	3.27	3.39
Mn	0.94	0.0022
Na	3.54	5.06
NH_4	<0.02	43.1
NO_3	0.58	<0.02
Pb	1.16	0.0007
PO_4	<0.05	49.1
SiO_2	22.7	21.6
SO_4	216	<0.05
U	0.0043	<0.0002
Zn	64.5	0.086

Pb and Cd are too low in mass concentration for phase identification. Although they are not metals of concern at this site, Mn, Cu, Al and U are also being reduced from the ppm/subppm level to the ppb level or below detection (Table 1). Therefore, biological reduction, precipitation, pH buffering and surface chemi-adsorption are all acting in this PRB.

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