

REMEDIATION OF GROUNDWATER CONTAMINATED WITH ZN, PB AND CD USING A PERMEABLE REACTIVE BARRIER WITH APATITE II¹

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Abstract. Phosphate-Induced Metal Stabilization (PIMS) using 100 tons of the reactive media, Apatite IITM [Ca_{10-x}Na_x(PO₄)_{6-x}(CO₃)_x(OH)₂ where x < 1], was used in a permeable reactive barrier (PRB) to treat shallow alluvial groundwater from acid mine drainage. The groundwater is treated *in situ* before it enters the East Fork of Ninemile Creek, a tributary to the Coeur d'Alene River. Microbially-mediated sulfate reduction and the precipitation of sphalerite (ZnS) is the primary mechanism occurring for immobilization of Zn and Cd. Precipitation of pyromorphite Pb₁₀(PO₄)₆(OH,Cl)₂ is the most likely mechanism for immobilization of Pb. Precipitation occurs on the original Apatite II grains. Emplaced in January of 2001, the PRB has continuously reduced the concentrations of Cd and Pb about 1 mg/L to below detection (2 mg/L), has reduced Zn to less than 0.1 mg/L, and has reduced sulfate and nitrate to below 0.05 mg/L, removing about 10,000 lbs of Zn, 200 lbs of Pb, and 100 lbs of Cd. About 90% of the immobilization is occurring in the first 20% of the barrier with loadings up to 25% Zn by weight of Apatite II.

Additional Key Words: phosphate, acid mine drainage.

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Introduction

Phosphate-Induced Metal Stabilization (PIMS) has been investigated as a remediation technology for heavy metals, particularly for acid mine drainage. The objective of this study was to implement and evaluate the performance of a PIMS permeable reactive barrier with respect to acid mine drainage in northern Idaho. In the Coeur d'Alene Mining District of northern Idaho, zinc (Zn) is the contaminant of concern with respect to aquatic life, and lead (Pb) and cadmium (Cd) are the contaminants of concern with respect to human health and wildlife. In 1995, the Success Mine and Mill site was identified as the largest remaining metals loader in the Ninemile Creek drainage (Golder, 2000), an upper basin tributary to the South Fork of the Coeur d'Alene River, which ultimately flows into Lake Coeur d'Alene. The Success site contributed approximately 37% and 87% of the total metals load to this drainage at high and low discharge periods, respectively (Golder, 2000). The source of the metals is groundwater discharge from the Success waste rock pile to the East Fork of Ninemile Creek (EFNC). A permeable reactive barrier was chosen to treat waters as they emerged from this source as opposed to treating the large volume of material in the waste pile Fig. 1).

Permeable reactive barriers (PRBs) consist of a water permeable material with specific chemical reactivities towards one or more chemical constituents via mechanisms such as adsorption (Bowman, 2003), exchange, oxidation-reduction (Benner *et al.*, 1997; Goldstein *et al.*, 2000; Naftz *et al.*, 2000; Puls *et al.*, 1999; Starr and Cherry, 1994; Tratnyek *et al.*, 1997), or



Figure 1. Success Mine tailings pile with the East Fork of Ninemile Creek in foreground. The PRB is between the pile and the creek.

precipitation (Bostick *et al.*, 1999; Conca *et al.*, 2000; Conca *et al.*, 2003; Fuller *et al.*, 2002; Matheson *et al.*, 2002; Wright *et al.*, 2004a). Previous work has shown that apatite minerals are effective at stabilizing metals and radionuclides and can be emplaced easily into a PRB (Chen *et al.*, 1997a,b; Eighmy *et al.*, 1997; Ma *et al.*, 1993, 1995; Manecki *et al.*, 2000; Ruby *et al.*, 1994; Stanforth and Chowdhury, 1994; Wright *et al.*, 2004a,b; Wright *et al.*, 2005; Xu and Schwartz, 1994; Zhang *et al.*, 1998).

Apatite minerals form naturally and are stable across a wide range of geologic conditions for hundreds of millions of years (Nriagu, 1974; Wright, 1990a,b). Work by Wright and others (Wright *et al.*, 1984; Wright *et al.*, 1987a,b; Wright *et al.*, 1990) investigated the trace element composition of fossil apatite (teeth and bones) and sedimentary phosphorite deposits over geologic time, and found that sedimentary and biogenic apatites deposited in seawater concentrate metals and radionuclides from the seawater to millions of times the ambient concentration, and lock them into the apatite structure for up to a billion years with no subsequent desorption, leaching or exchange, even in the face of diagenetic changes in the pore water chemistry, pH, temperatures over 500° C, and tectonic disruptions. Over 300 apatite minerals exist, with elements from the entire periodic table replacing calcium, phosphate, and hydroxide in the fundamental apatite crystal structure (Skinner, 1989; Wopenka and Pasteris, 2005) with solubility products (K_{sp}) varying from about 10^{-20} to 10^{-150} (Nriagu, 1974; Manecki *et al.*, 2000).

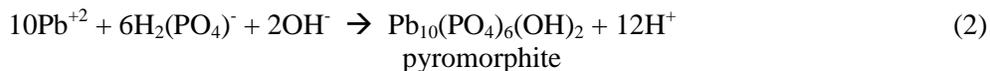
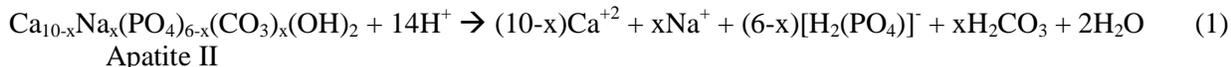
Materials and Methods

Water samples were collected in the field during regular monitoring activities and sent to approved EPA laboratories for major, minor and trace element analyses, using Inductively-Coupled Plasma Mass Spectrometry (ICP/MS) and Ion Chromatography (IC), respectively, for metal and anion concentrations in waters. In particular, alkalinity, CO_3^{2-} , HCO_3^- and CaCO_3 were measured using Method 2320B, Cl, F, nitrate-N, and SO_4^{2-} were measured using Method 300.0, NH_4 was measured using Method 350.1, nitrate + nitrite was measured using Method 353.2, total, dissolved, and ortho- phosphate were measured using Method 365.2, total Kjeldahl N was measured using Method 351.4, and Cd, Fe, Mn, Pb, Zn, K, Mg, Na, and Si were measured using Method 200.7. The pH was determined on samples as they were collected in the field using a Beckman pH Meter with a combination electrode calibrated with traceable standard solutions. Various portable field probes were used to periodically test waters in the field for dissolved O_2 and Eh by personnel from the Idaho National Laboratory (INL) courtesy of Neal Yancy, INL.

Sequestration Mechanisms in Apatite

The reactive media used is Apatite II™ (U.S. Patent #6,217,775), a biogenically-precipitated apatite material derived from fish bones with a general composition of $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$ where $x < 1$. This material stabilizes a wide range of metals, by forming new stable phosphate minerals and other phases with low solubility products (K_{sp}), e.g., pyromorphite (Pb-apatite) $K_{sp} < 10^{-80}$ (Geochem, 1994; Nriagu, 1974; Ruby, 1994; Manecki *et al.*, 2000). In the presence of a pre-existing apatite surface that provides nucleation sites, the kinetics of the metal-phosphate precipitation is extremely rapid (Koeppenkastrop and De Carlo, 1990; Lower *et al.*, 1998). Since the solubility of the initial Apatite II is also low, $\sim K_{sp} = 10^{-20}$, it will remain in the environment for a long time to treat metals as they enter the system without causing phosphate loading.

Apatite II works by four different processes depending upon the metal, concentration and aqueous chemistry. First, 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 provides the surface for heterogeneous nucleation via a two-step process (Lower *et al.*, 1998; Wright *et al.*, 1995):



The second process is pH buffering, also shown in reaction 1. Reaction 1 does not necessarily lead to reaction 2. However, whenever Pb^{+2} is in solutions contacting the apatite, the apatite provides a small but constant supply of phosphate to solution to induce reaction 2. This excess dissolution leads to the strong pH buffering exhibited by Apatite II under acidic conditions. Apatite II buffers the pH to neutral (6.5 to 7) 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. The third process is surface chemi-adsorption. Apatite II is an excellent material for non-specific metal adsorption, particularly of the transition metals, through its uncompensated phosphate and hydroxyl surface groups (Conca, 1997).

The fourth process is biological stimulation and is the primary mechanism of Zn sequestration in the Success Mine PRB. Apatite II supplies both P and readily-bioavailable organics at low but optimal concentrations for stimulating microbial communities (Martinez *et al.*, 2005), especially sulfate and nitrate reducers, and those important to biodegradation of contaminants such as TNT and perchlorate. Apatite II contains between 30% and 40% organics by weight, mostly collagen with varying amounts of more soluble proteins, fats and lipids, such as cholesterol, that remain after the fish bone processing steps (Martinez *et al.*, 2005). The organics slowly leach out from the capillary pores and other microporosity of the Apatite II, and the equilibrium P concentration from dissolution of the Apatite II is in the mg/L range (usually between 1 and 10 mg/L, but as low as 0.5 mg/L and as high as 50 mg/L depending upon pH and major solution chemistry). Martinez *et al.* (2005) hypothesized that the Apatite II reduces metal toxicity that might otherwise prevent or limit microbial activity. The 100 tons of Apatite within the PRB can sustain these biologically-favorable conditions for 10 to 20 years depending upon flow rate and solution chemistry.

Within the Success Mine PRB, sulfate reduction using organic carbon from the Apatite II can be represented as (Benner *et al.*, 1997; Scherer *et al.*, 2000):



The CH_2O represents the organic carbon from the Apatite II that serves as both electron donor and carbon source for the sulfate reducers (Scherer *et al.*, 2000). There are no other sources of organics within this system. The sulfate reduction within the Success Mine PRB is being microbially-mediated by *Enterococci*. The solubility of the sphalerite, represented by the reverse reaction in reaction 4, is still very low, $K_{sp} < 10^{-11}$ (Geochem, 1994), therefore, the stability of the resulting product from a remediation standpoint is very good, and concentrations of Zn and S exiting the PRB should be very low, as is the case for the Success Mine PRB.

Sulfate reduction (reaction 3) also provides strong pH buffering in this particular system in addition to apatite dissolution.

Geologic Setting

The Success Mine and Mill site is located within the Coeur d'Alene Mining District of northern Idaho, in Shoshone County, approximately five miles northeast of Wallace and is underlain by the Belt series of Precambrian age (Hobbs *et al.*, 1965). The Success site, incorporating the mine, a ~300,000 cubic yard tailings and waste rock pile and mill foundations, covers an area of about 10 acres within a steep-sided narrow canyon drained by the East Fork of Ninemile Creek (EFNC). The EFNC is a tributary to Ninemile Creek, which is in turn a tributary to the South Fork of the Coeur d'Alene River. The site is situated in a relatively wide (400 feet), almond-shaped alluvial flat on the east side of an otherwise narrow V-shaped canyon. The waste pile (1,200 feet in length, about 150 feet high with side slopes of up to 40 degrees) occupies the lower half of the almond-shaped flat (SAIC, 1993). There is 20 to 60 feet of ground between the creek and toe of the pile. The EFNC, with a gradient between 7 to 8% from 3,790 feet to 3,560 feet above sea level across the site, flows into the main stem of Ninemile Creek about 1.3 miles downstream of the Success site. The confluence of Ninemile Creek with the South Fork of the Coeur d'Alene River occurs 4.3 miles down-stream of Success. The EFNC basin receives an average of 50 inches of precipitation per year. The average annual flow for the EFNC is estimated at 15.8 cfs with a 2-year peak flow of 169 cfs, a 50-year peak flow of 424 cfs and a 100-year peak flow of 480 cfs. Peak flows typically occur in April and May (SAIC, 1993).

The Success Mill and Mine site, discovered in 1885, was mined from 1886 and 1932 and reworked from 1934 to 1956, producing about 790,000 tons of ore grade material. In 1993, the EPA completed a time-critical response action at Success that involved relocation of the EFNC into an armored 500-year channel (Fig. 1) and berm protection of the tailings/waste rock pile from further mass erosion into the EFNC (U.S. EPA, 1993). The Idaho Department of Environmental Quality (DEQ) also installed surface water diversions around the pile. After being identified by DEQ as the largest remaining metals loader in the Ninemile Creek drainage, a technical team comprised of state, county, mining company, citizen, federal, tribal and consultant representatives evaluated several response actions and decided on emplacement of a PRB as the preferred alternative since it best met the evaluation criteria, represented a timely response action, could be completed with existing funds and provided an opportunity to complete a full-scale field project that would not preclude other response actions in the future (Calabretta *et al.*, 2001).

Results and Discussion

PRB installation

Pre-installation site investigations included excavation of test pits, installation of piezometers and five deep/shallow groundwater monitoring well pairs at the toe of the tailings pile, water quality and soil sampling, slug testing of the wells and water level monitoring (Calabretta *et al.*, 2001). Bedrock, a quartz monzonite (Hobbs *et al.*, 1965), was encountered between 16.5 and 22.5 feet below ground surface with an average downgradient surface slope of 7.5%. The unconsolidated material above bedrock comprises fill material, including a 2 to 7-foot thick mixed tailings/alluvium layer, overlying a poorly sorted alluvium. Soils are contaminated with tens of thousands of mg/kg of metals and concentrations of Cd, Pb, and Zn in groundwater

between the tailings pile and the EFNC average 0.5, 1 and 100 mg/L, respectively, significantly exceeding drinking water and aquatic life criteria. Our performance goals were to reduce the Pb and Cd concentrations to below 0.015 mg/L, and Zn to below 0.5 mg/L.

Over the lower portion of the site, where the tailings pile is located within 60 feet of the creek, the contaminated groundwater within the alluvial aquifer discharges directly to the creek. The hydraulic conductivity of the alluvial aquifer averaged 1.7×10^{-3} ft/s [0.61×10^{-3} m/s] (TerraGraphics, 1998; Golder, 2000). The hydraulic conductivity of the shallow bedrock averaged 5.6×10^{-5} ft/s [2×10^{-5} m/s]. There is between 3 and 100 gpm of shallow groundwater that flows out of the alluvial aquifer at the downgradient end of the site with a strong seasonal dependence (Golder, 2000).

The PRB design included construction of a 1,450-foot long pressure-grouted wall between the waste pile and the EFNC (Golder, 2000) extending vertically from about 2 to 3 feet above the spring groundwater high down into the top foot of the bedrock. A hydraulic drain was included just below the creek water level on the waste pile side of the wall, to direct the groundwater that backs up behind the grout wall towards and through the PRB, and to minimize the flow of surface water into the shallow groundwater system. A 13.5-foot high, 15 foot wide by 50 feet long PRB vault with two separately plumbed cells (East and West) was poured into rebar forms using Type V (corrosion resistant) Portland cement.

The vault was designed with an inflow port, two baffled PRB treatment cells (consisting of 5 connected chambers each) and two outflow ports with a head drop of 7.5 feet from the inflow. The plumbing was installed inside the vault and about 108 cubic yards of Apatite II (about 100 tons at \$300/ton) were placed within the two cells. The West cell has 100% Apatite II and the East cell has 50% ApatiteII/50% gravel (Fig. 2).



Figure 2. Installation of the Apatite II in the baffles of the PRB vault.

Cell dimensions measured about 8 feet in height, 6.5 feet in width and 45 feet in length. A compartment containing clean, rounded gravel was designed as the front compartment to the two PRB treatment cells. Groundwater flowing into the vault through the inlet flows downwards through the gravel and enters the two PRB treatment cells at their base. The surface of the PRB vault was covered with steel plates with manhole access to the inflow and outflow ports. Butterfly valves were installed to be able to control flow. The vault outflow discharges to the EFNC via a rock apron outfall. Construction was completed between September 2000 and January 2001 using traditional trenching and earth-moving equipment.

Monitoring and Performance

Monitoring began in January 2001 and average results from the entire PRB are presented in Table 1. East and West cells behaved very similarly with respect to metal removal and the results in Table 1 are an average of the two cells. Dissolved metals are reduced to the performance goals and the pH is buffered to 6 - 7. The PRB has sequestered about 100 lbs of Cd, 200 lbs of Pb and 10,000 lbs of Zn since it was emplaced and is estimated to last about ten more years based upon feasibility results (TerraGraphics, 1998) and the present state of the barrier.

Figure 3 is a cross-section through the PRB showing conditions measured during July of 2003. Portable probes were used to measure pH, Eh (oxidation/reduction potential), dissolved oxygen (DO), temperature, and conductivity at various points within the system (courtesy of Neal Yancy, INL). Oxygen probes gave DO concentrations of between 0.1 and 0.3 mg/L within the barrier, and over 4.0 upgradient and downgradient of the barrier. The Eh values within the first cell of the barrier were over +550, while most of the barrier interior was between -100 and -300. The pH rises to neutral in the first chamber of the barrier. Lead and Cd disappear completely from solution within the first chamber, while Zn concentrations decrease from chamber to chamber, finally dropping to about 0.1 mg/L or below before exiting the barrier. The Mn, Cu, Al and U concentrations are also being reduced to the ppb level or below detection.

Bacteria sampling, performed by Golder and Associates (Calabretta *et al.* 2001) was carried out at: 1) the EFNC upstream of the PRB; 2) the PRB inflow; 3) the PRB outflow; and 4) just upstream of the East Fork – West Fork confluence at the DobsonPass culvert where the greatest possibility exists for the public to come in contact with water that has exited the PRB. The water samples were analyzed for *Ecoli*, *Enterococci*, *Pseudomonas* and *Salmonella*. All samples were non-detect at all points except for *Enterococci* at the PRB outflow in March 2001, which was measured at 16,000 MPN/100ml, where MPN represents the most probable number. This number decreased rapidly once the outflow left the area of the PRB so that it was non-detect by the time water reaches the East Fork – West Fork confluence at the Dobson Pass culvert. The recreational guideline for *Enterococci* in fresh water is 30 MPN/100ml. Culturing of samples from within the barrier is ongoing. However, this result was only obtained during the first sampling event in 2001. All later samplings in 2002, 2003 and 2004 showed non-detects even for *Enterococci* at the PRB outflow.

Total dissolved P upstream of the PRB is below 0.04 mg/L. Phosphorus loading to the creek from the PRB was found to be between 2 and 20 mg/L total dissolved P, mostly as orthophosphate, at 5 to 30 gpm flow. This is similar to the background range observed in other drainages downstream such as the Coeur d'Alene River at Pinehurst (20 to 130 mg/L total dissolved P) and St Joe at Calder (3 to 10 mg/L total dissolved P).

Initial MINTEQ modelling indicate pyromorphite and sphalerite (ZnS) as the most stable phases within the barrier with regard to 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. Solids collected from the first chamber of the PRB cells show a whitish solid covering most of the original Apatite II and show little residual organics left on the Apatite II. This solid is primarily composed of Zn, Ca, P, and S and is a mixture of sphalerite and recrystallized chlorapatite, according to XRD and as seen with SEM (Fig. 4). This observation is consistent with reactions 1 through 4. Dissolution of the Apatite II (both the apatite mineral and the organic phases) and precipitation of secondary sulfide and apatite phases are combining to remediate this groundwater. Because Pb and Cd occur in concentrations between 100 and 1000 times lower than Zn, no discrete Pb or Cd phases have been identified in hand specimens or with SEM.

Compared to the front two cells of the PRB, the Apatite II in the rear three cells is relatively unreacted, does not exhibit secondary mineral coatings, and still has a large compliment of the original organics. Visual inspection estimates that less than 30% of the Apatite II is spent. When breakthrough from the PRB with respect to Zn does occur, the spent Apatite II can be replaced as it will not be a hazardous waste (spent Apatite II from previous studies passed EPA TCLP tests) and can be disposed for less than \$20/ton. The first chamber of the PRB has removed so much metal that its hydraulic conductivity has declined and removal is planned at the time of publication. The chamber can be re-filled or left empty to serve as a sediment trap for the subsequent chambers.

Table 1. Dissolved Metal Concentrations Entering and Exiting the Apatite II PRB

Date	Entering Barrier ($\mu\text{g/L;ppb}$)				Exiting Barrier ($\mu\text{g/L;ppb}$)			
	pH	Cd	Pb	Zn	pH	Cd	Pb	Zn
1/20/01	---	---	---	---	7.0	< 2	< 5	14
3/23/01	4.5	333	1,230	44,700	6.0	< 2	< 5	27
6/1/01	5.0	413	1,400	58,500	7.0	8	65	900
8/20/01	4.5	379	1,290	53,700	6.5	6	11	775
10/27/01	5.0	437	1,110	71,300	6.5	< 2	< 5	74
1/10/02	5.0	779	1,210	116,000	6.5	< 2	< 5	66
6/27/02	4.8	726	1,450	57,230	6.9	< 2	< 5	243
8/02/02	4.2	430	1,185	64,600	7.1	< 2	< 5	83
10/19/02	4.5	414	1,030	68,350	6.5	< 2	< 5	69
11/10/02	4.5	428	869	65,600	6.5	< 2	< 5	39
12/16/02	4.5	474	926	83,950	6.5	< 2	< 5	91
2/6/03	4.5	664	983	101,000	6.8	< 2	< 5	46
3/14/03	4.5	650	1,190	48,700	6.6	< 1	< 1	55
4/23/03	4.5	318	513	50,300	6.5	< 2	< 5	36
5/29/03	4.5	477	869	71,300	6.8	< 2	< 5	20
6/26/03	5.5	809	1,310	122,000	6.9	< 2	< 5	19
7/1/03	4.5	749	1,350	146,900	6.8	< 2	< 5	59
10/3/03	4.6	587	1,330	86,800	7.0	< 2	< 5	<5
3/30/04	5.2	404	497	64,500	6.9	< 2	< 5	95
6/9/04	4.9	436	658	68,000	6.9	< 2	< 5	34

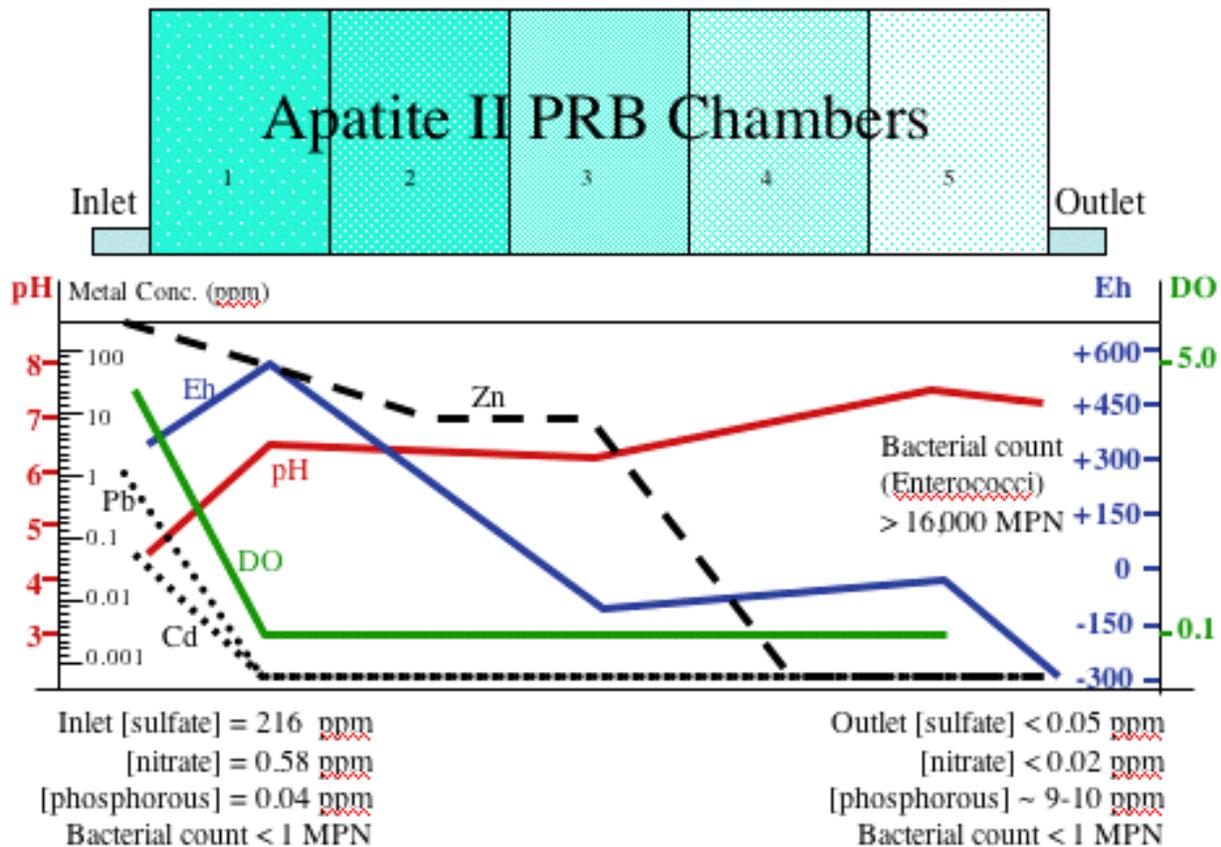


Figure 3. Schematic of Apatite II PRB and the chemistry within the west cell.

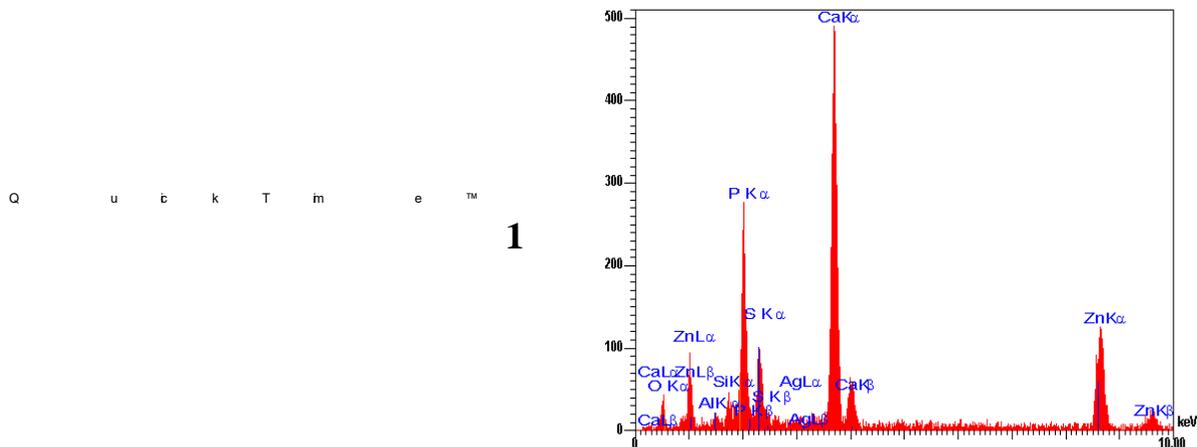


Figure 4. Photomicrograph of Apatite II from the first chamber of the PRB (Fig. 3) showing biologically-mediated formation of micron-sized ZnS (sphalerite) crystals forming on surface of the Apatite II (image is 200 mm in width). EDS analysis of crystal labeled **1** at right.

Summary

Apatite II was selected for use within a permeable reactive barrier (PRB) for a voluntary CERCLA non-time critical removal action completed by the Silver Valley Natural Resource Trustees at the Success site, in northern Idaho. The 13.5-foot high, 15 foot wide by 50 feet long PRB vault with two cells was placed between a 300,000 cubic yard tailings/waste rock pile and the East Fork of Ninemile Creek to reduce metal loading downstream by capturing and treating groundwater at the toe of the pile. The Apatite II PRB has been operating successfully at the site since January 2001, and has reduced the concentrations of Cd (from hundreds of ppb) and lead (from thousands of ppb) to below detection (2 µg/L or ppb), has reduced zinc from 100 ppm to near background in this region (about 100 µg/L or ppb), and has reduced sulfate and nitrate to below detection (50 µg/L), prior to discharge to surface water. So far, during the 4-year operation, the PRB, filled with about 100 tons of Apatite II, has removed over 10,000 lbs of Zn, over 200 lbs of Pb, and over 100 lbs of Cd, and has buffered the pH to between 6.5 and 7 from an influent pH averaging about 4.5. The groundwater PRB treatment system is performing as designed.

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