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PIMS: an Apatite II Permeable Reactive Barrier to Remediate Groundwater Containing Zn, Pb and Cd

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ABSTRACT

This paper describes the use of Phosphate-Induced Metal Stabilization (PIMS) employing the reactive media, Apatite II, in a subsurface permeable reactive barrier (PRB), to treat groundwater containing elevated levels of zinc, lead, cadmium, sulfate and nitrate at the Success tailings/waste rock pile. The impacted groundwater is treated *in situ* before it enters the East Fork of Ninemile Creek, a tributary to the Coeur d'Alene River. Laboratory feasibility studies demonstrated the greater effectiveness and lower cost of Apatite II relative to eight other reactive media. As a result, Apatite II was selected for use in a voluntary non-time critical CERCLA removal action completed by the Silver Valley Natural Resource Trustees (SVNRT) at the Success Mine and Mill site in northern Idaho. The emplaced PRB has been operating successfully since January of 2001, and has reduced the concentrations of cadmium and lead generally to below detection (2 μg/L or ppb), has reduced zinc to near background (about 100 μg/L or ppb), and reduced sulfate and nitrate to below detection (50 μg/L or ppb). The PRB, filled with 100 tons of Apatite II (@$350/ton), has been in operation for over two years and has removed over 6,000 lbs of Zn, both sorbed onto the Apatite II and as ZnS, over 100 lbs of Pb as pyromorphite, and over 50 lbs of Cd. It is hoped that projects of this kind will demonstrate the ease and cost-effectiveness of using inexpensive reactive media to treat sources of metal loading that are difficult or costly to remove, e.g., very large sources for which there is no landfill space available, sources located beneath infrastructures, sources that would require significant disruption of communities, industries or services, and tailings piles/adit discharges located in remote areas with limited access.

INTRODUCTION

In the Silver Valley Mining District of northern Idaho (also known as the Coeur d'Alene Mining District), Zn is the contaminant of concern with respect to aquatic life, while Pb is the contaminant of concern with respect to human health and wildlife, such as geese and swans that feed in sediments containing elevated levels of Pb. In 1995, the Success Mine and Mill site was identified as the largest remaining metals loader in the Ninemile Creek drainage. Ninemile Creek is an upper basin tributary to the South Fork of the Coeur d'Alene River, which ultimately flows into Lake Coeur d'Alene. Based on data collected by the Idaho Department of Environmental Quality (DEQ) in 1994 and 1995, the Success site contributed approximately 37% and 87% of the total metals (cadmium, lead and zinc) load at high and low discharge, respectively. The primary source of the metals loading was identified as groundwater discharge from the toe of the Success tailings/waste rock pile to the East Fork of Ninemile Creek (Golder, 2000b). Up to this time, the removal of metals sources within the floodplains and streams of the Silver Valley has relied primarily on excavation of impacted materials followed by transport of these materials to hydraulically isolated repositories. The purpose of this study was: 1) to investigate in the laboratory the performance of alternative reactive barrier materials for use in a permeable reactive barrier (PRB) at the Success Mine and Mill site; 2) to choose a reactive media for a PRB and emplace the PRB to demonstrate a reduction in metals loading to the East Fork of Ninemile Creek (EFNC); and, 3) to monitor the effectiveness of the PRB to reduce the concentrations of Zn, Pb and Cd in groundwater flowing through the PRB.

BACKGROUND

The results of previous and ongoing work demonstrate that stabilization of contaminated soils and groundwater by apatite minerals has the potential to be a successful and widely applicable remediation strategy for metals and radionuclides. Utilizing apatite minerals for remediation uses 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; 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 at least 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 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 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
$Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$	-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

PREVIOUS WORK

The PRB Concept

Permeable reactive barriers (PRBs) to particular chemical contaminants consist of a water permeable material with specific chemical reactivities towards one or more chemical constituents via mechanisms such as adsorption, exchange, oxidation-reduction, or precipitation. These barriers can have varying ranges of specificity, e.g., adsorption of specific 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.*, 1999), or overall reduction of the system by zero valent iron, other iron phases, or microbial activity (Blowes *et al.*, 1997; Tratnyek *et al.*; 1997; Puls *et al.*, 1999).

PRBs can be emplaced physically by trenching and replacing the natural substrate with reactive media to form a wall of new material, can be emplaced by mixing or injecting reactive components into the substrate, or can be emplaced in subsurface boxes or cartridges where the reactive media can be replaced as needed. Either way, the migrating contaminant plume encounters the reactive material in the barrier, the contaminant is sequestered, altered or degraded, and the water moves on through the barrier and exits the system, leaving the contaminant sequestered in the reactive media (Figure 1). Successful emplacement of a PRB requires sufficient knowledge of both the hydraulic and chemical nature of the system. Impermeable barriers and PRBs can be used in combination to control both the hydrologic and chemical aspects of the treatment zone. Funnel and gate systems, or other systems that use impermeable barriers to channel groundwater flow, are well suited for these applications (Starr and Cherry, 1994).

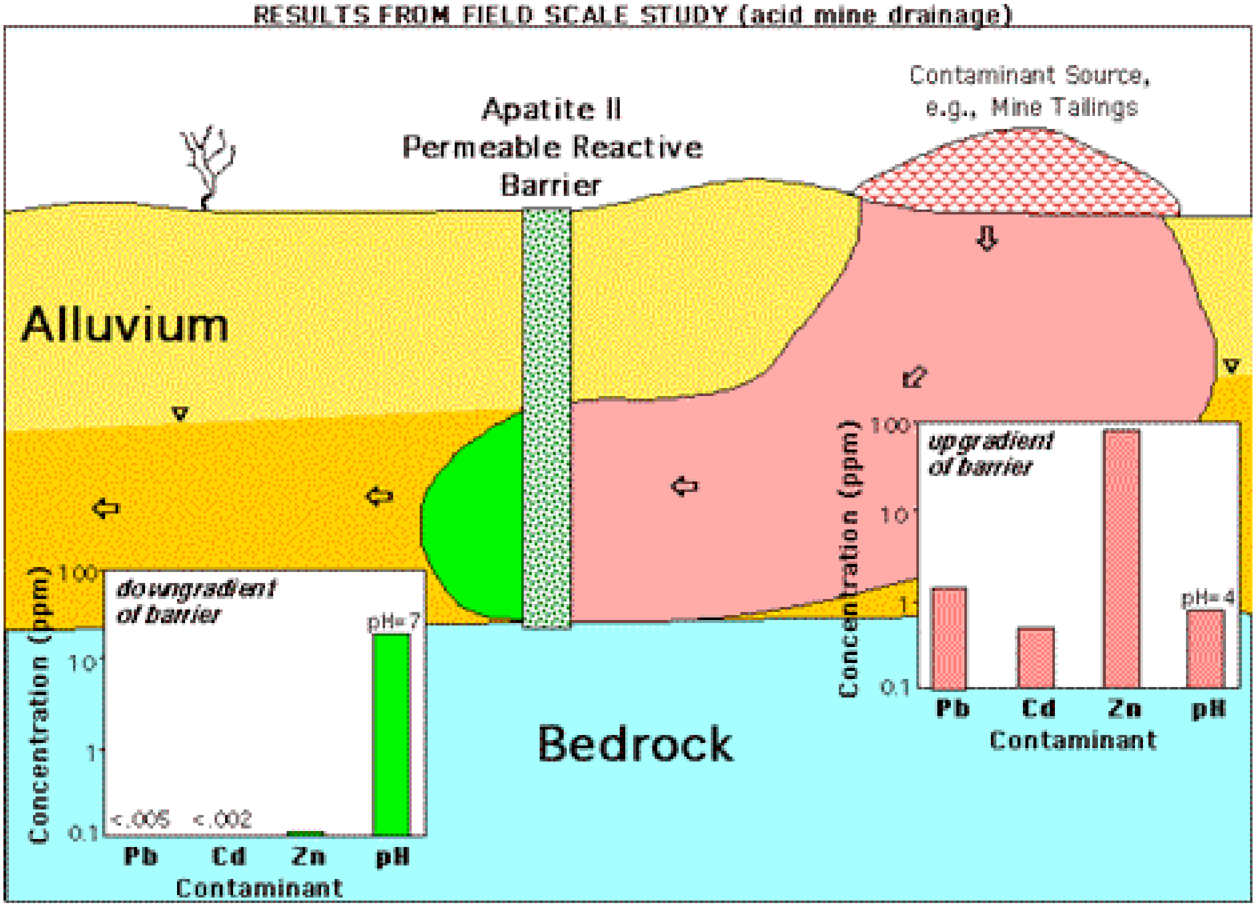

Figure 1. Permeable reactive barrier (PRB) concept illustrated with actual field results.

PRB Reactive Media

Materials used in the field must be effective, inexpensive and readily available in multiple-ton quantities to be able to treat large volumes of water, or soil. Some of the candidate materials that have been researched include zero valent iron, zeolites, apatites, periclase (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 almost exclusively 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, 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).

The PRB reactive media chosen for this site 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. Apatite II is also an efficient non-specific surface adsorber and is available in multiple-ton quantities at low cost (U.S. Patent#6,217,775). 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 (from ppb to ppm levels of PO_4^{3-} resulting in no phosphate loading or eutrophication) 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.

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 nominal composition of Apatite II is $Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$ where $x < 1$. For Pb, the overall reaction can be summarized as follows (adapted from Ma et al., 1993):

$$\underset{\text{Apatite II}}{Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2} + 10Pb^{2+} + x(H_2PO_4)^- \rightarrow \underset{\text{pyromorphite}}{Pb_{10}(PO_4)_6(OH)_2} + (10-x)Ca^{2+} + xNa^+ + xH_2CO_3 \tag{1}$$

which is actually a two-step dissolution reaction of the Apatite II and precipitation of pyromorphite:

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

$$10Pb^{2+} + 6H_2(PO_4)^- + 2OH^- \rightarrow \underset{\text{pyromorphite}}{Pb_{10}(PO_4)_6(OH)_2} + 12H^+ \tag{3}$$

The degree of protonation of the phosphate and carbonate in the intermediate reactions depends upon the pH. The above example is for the range of acid mine drainage, pH between 3 and 6. Reaction (2) does not usually lead to reaction (3). However, whenever Pb^{2+} is in solutions contacting the apatite, the apatite provides a constant supply of phosphate to solution to induce reaction (3). This excess dissolution leads to the strong pH buffering exhibited by Apatite II as a result of reaction (2).

Similar overall reactions occur for U, Ce, Pu and other metals for which precipitation is the primary mechanism for removal from solution. The solubility of the new phase controls the equilibrium concentration of the metal in solution. Therefore, equilibrium 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 results 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). However, for Zn, Cd and other transition metals, adsorption or precipitation into non-apatite phases are primary mechanisms, therefore, the performance with respect to these metals depends upon the adsorption characteristics of the apatite. Just as the 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 (Langmuir, 1997). 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 adsorption properties of the Apatite II. However, for adsorption-controlled systems, the equilibrium concentration will be more dependant upon solution chemistry, surface properties, grain size, degree of crystallinity, and competing ions. As described below, most other apatites will not effectively adsorb the transition metals.

Other processes and remediation technologies for other contaminants are not inhibited by apatite treatment, e.g., agricultural uses, landfarming or windrowing will not compromise this treatment, and metal-stabilization by apatite treatment will not affect vapor stripping or bioremediation of organics from the same soils in a mixed-waste system. For applications in which both chemical stabilization and physical solidification are desired (in landfills, for example), apatite can be combined with grout for improved stabilization performance. Apatite is also ideal as an additive to disposal facility liners, and can be used with other additives, such as bentonite or zeolite. Finally, this treatment is possible using existing emplacement technologies, e.g., auguring or mixing into contaminated soils, slurry injection, excavation and backfill, or above-ground treatment of contaminated groundwater. At present in the United States, Phosphate-Induced Metal Stabilization (PIMS) using Apatite II achieves total treatment costs of about \$23/treated ton of lead (Pb)-contaminated soil, or \$40/1,000,000 gallons of water contaminated with 1 mg/L Pb, based on actual field implementation costs during corrective actions.

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 (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., 1999). Apatite II exhibits all of these properties. Figures 2 and 3 are High-Resolution Transmission Electron Microscopy images (HR-TEM; Lu et al., 2001) comparing the structural properties of the Apatite II and cow bone. The cow bone is a less effective phosphate material for remediation of metals because of its higher crystallinity (results were similar for bone char and for cow bone). As will be seen below, 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.

THE SUCCESS MINE AND MILL SITE

Site Description and Background

The Success site is located within the Coeur d’Alene Mining District of northern Idaho, in Shoshone County, approximately five miles northeast of Wallace (Figure 4). The project site, incorporating the mine, a 200-350,000 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 Success 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

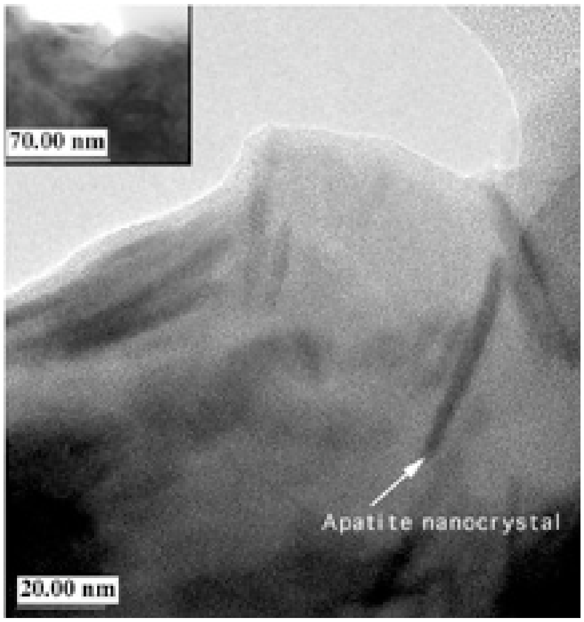

Figure 2. HR-TEM image of Apatite II showing the general amorphous nature of the matrix with random nanocrystal inclusions of crystalline apatite embedded throughout.

feet high with side slopes of up to 40 degrees) occupies the lower half of the almond-shaped flat. At present, there is between 20 and 60 feet of ground between the creek and toe of the pile. The EFNC headwaters originate three miles upstream of the Success site at the Tamarack Saddle, about 5,300 feet above mean sea level (MSL). The EFNC flows into the main stem of Ninemile Creek about 1.3 miles downstream of the Success site at an elevation of 3,150 feet above MSL. The confluence of Ninemile Creek with the South Fork of the Coeur d'Alene River occurs 4.3 miles down-stream of Success at about 2,700 feet above MSL. Within the portion of EFNC which passes through the site, the stream elevation drops from 3,790 feet to 3,560 feet above MSL at a gradient of between 7 to 8% (Terragraphics, 1997). The current EFNC channel (modified by EPA in 1993) was designed by the Bureau of Reclamation to contain a 500-year flood but has limited aquatic/riparian habitat potential. This reach comprises an approximately 2,100-ft long trapezoidal channel with an approximately 10-foot bottom width, greater than 4-foot high 1H:1V side slopes and no usable floodplain. The EFNC basin receives an average of 50 inches of precipitation per year (Kasun, 1993). The average annual flow for the EFNC has been 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 (Kasun, 1993). Peak flows typically occur in April and May.

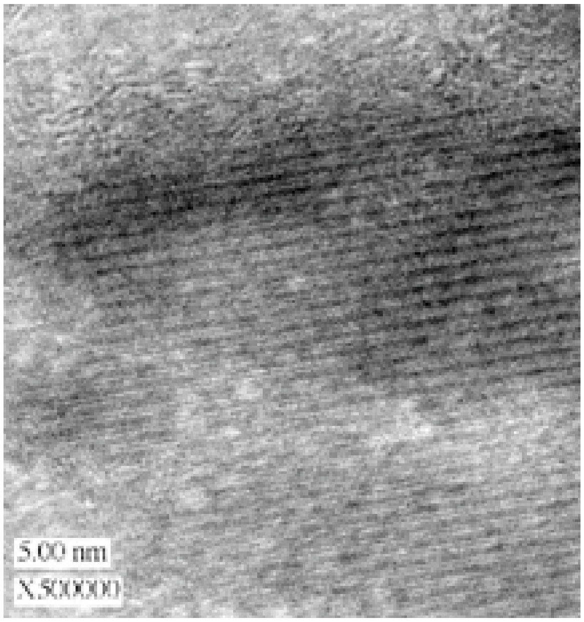

Figure 3. HR-TEM image of cow bone char showing the crystalline nature of the apatite.

The Success Mill and Mine site is owned by the Success Mining Company, an Idaho corporation since 1905, owned by about 625 shareholders. Discovered in 1885, mining at the site occurred between 1886 and 1932 (USGS, 2000). A 150-ton per day mill was built in 1906 and was upgraded to a 200-ton per day mill in 1907. Between 1934 and 1956 lessees reworked a portion of the tailings and waste rock pile for zinc. Records indicate that the mine produced 790,000 tons of ore grade material. The milling process concentrated the metals, primarily by crushing the ore, followed by jigging or screening to separate the denser, metal-bearing fraction. The mill byproducts (tailings) and waste rock were deposited downstream (south) of the mill site, on the eastern side of the EFNC. Assuming no mass erosion of tailings, approximately 666,000 tons of tailings (about 392,000 cubic yards assuming a 0.59 conversion factor) would have been produced at the site (SAIC, 1993). The current volume of tailings and waste rock remaining on-site is estimated to range between 200,000 to 350,000 cubic yards (Golder, 2000a). Historically, the tailings pile was in direct contact with the creek resulting in erosion, dissolution, and downstream transport of tailings. In 1993, the EPA completed a time-critical response action at Success that involved relocation of the EFNC into an armored 500-year channel (Figure 5) and berm protection of the tailings/waste rock pile from further mass erosion into the EFNC (US EPA, 1993). The Idaho Department of Environmental Quality (DEQ) also installed surface water diversions around the pile.

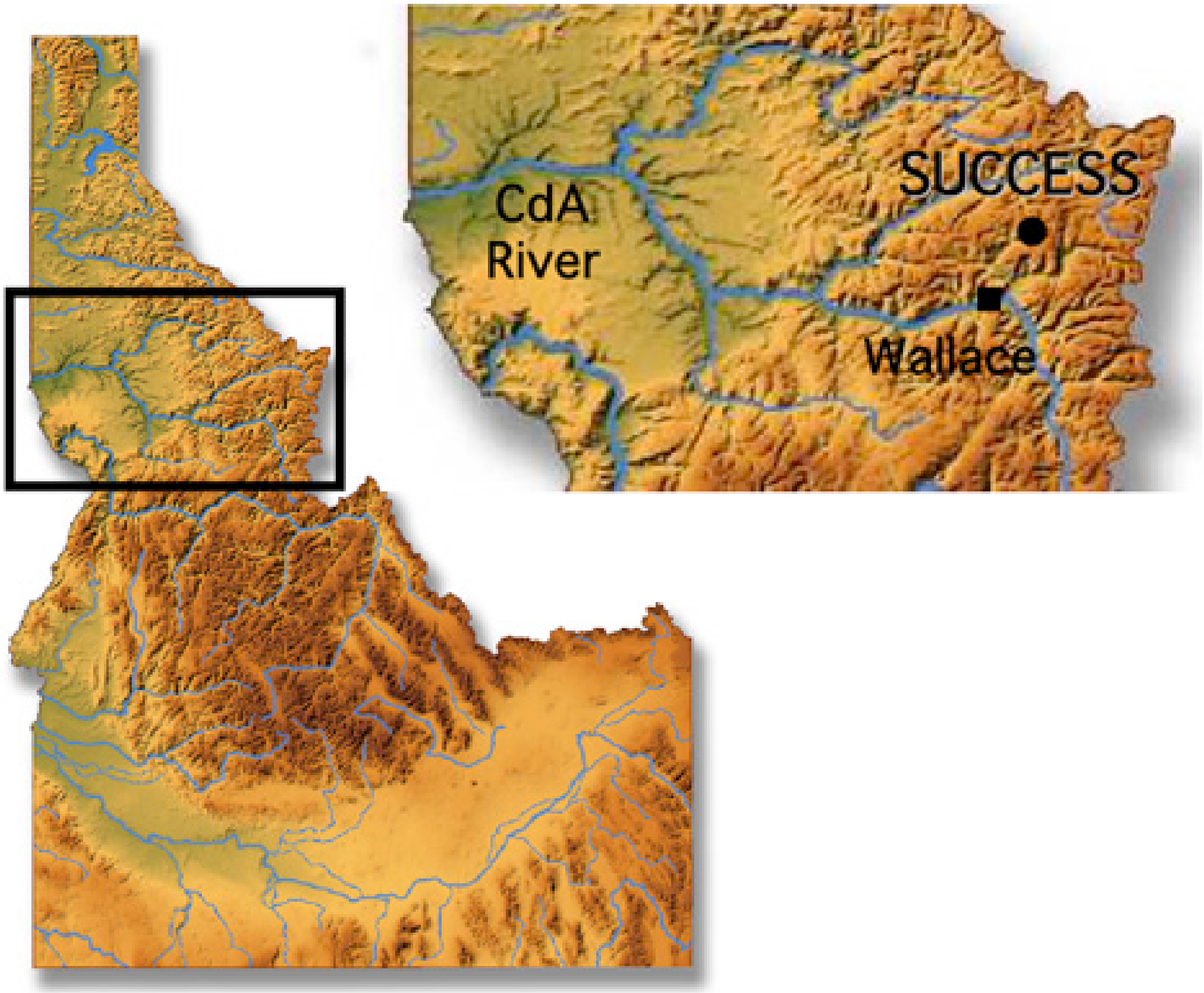

Figure 4. Location Map for the Success Mine and Mill Site, Idaho.

In 1995, the Success site was identified by DEQ as the largest remaining metals loader in the Ninemile Creek drainage, contributing approximately 37% of the total cadmium, lead and zinc at high flow, and 87% at low flow. The primary source of the metals loading was identified as groundwater discharge from the toe of the tailings/waste rock pile to the creek. 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 demonstration project that would not preclude other response actions in the future.

Reactive Media Selection for the PRB

Prior to selection of a reactive media for the Success site PRB, the metal-stabilization potential of reactive phosphates from different sources, along with other candidate media, were investigated. Studies used shallow alluvial groundwater collected from the Success site and containing elevated levels of Zn, Pb, Cd and Cu up to concentrations of 250 ppm, 10 ppm, 1 ppm and 20ppm, respectively. Reactive media were obtained from commercial sources from ton-batches that would be used in the field. These media included five different sources of apatite (three Apatite II formulations, phosphate rock and cow bone), iron-filings, compost/woodchip/gravel mixtures, two zeolites (Carbsorb and clinoptilolite), a polymer used in remediation of mine wastes (C-sorb), and activated charcoal.

Figure 5. Success Mine tailings pile with the East Fork of Ninemile Creek channel in foreground.

Flow-through column tests were used to evaluate the performance of the reactive media. These tests used polypropylene columns with micron-filter ends in which between 10 and 30 grams of each material was packed into the column to a bulk density similar to that expected in the field. Flow rates were 3ml/hr and gave average water residence times of between one and three hours depending upon the pore volume of each column. The densities of materials varied from 0.8 g/cm^3 for the Apatite II, to between 1.2 and 1.6 g/cm^3 for all other materials except for the iron filings, which was slightly over 4 g/cm^3. Water was introduced at the top of the sample, and collected as a function of the number of pore volumes (PV) of solution added, i.e., the volume of water approximately equal to that in the pore space of the material in the column at any one time. The effluents were filtered to 0.1 μm. These experiments were performed with the actual systems, e.g., contaminated groundwater as collected from the field, and with various reactive media as they would be purchased and emplaced in the field. Inductively-Coupled Plasma Mass Spectrometry (ICP/MS) and Potentiometric Stripping were used to analyze for metal concentrations in the groundwaters entering and exiting the columns. pH was determined on the effluent as it was collected using a Beckman pH Meter with a combination electrode calibrated with traceable standard solutions.

Results for column tests are given as plots of contaminant concentration in the effluent normalized to the influent, C/C$_0$, versus the volume of water passing through the column normalized to the weight of media in the column. This normalizes the columns so that they can be compared to each other on a weight basis and because these materials are purchased and emplaced on a weight basis. Breakthrough is usually taken to be when C/C$_0$ = 0.5, but significant sorption can still occur until the material is fully loaded. Also, after breakthrough of one metal occurs, the material can still sequester another metal via different mechanisms, e.g., Pb can continue to be immobilized through precipitation long after Zn breaks through the system, which has been observed in lab and pilot scale tests (Conca 1997).

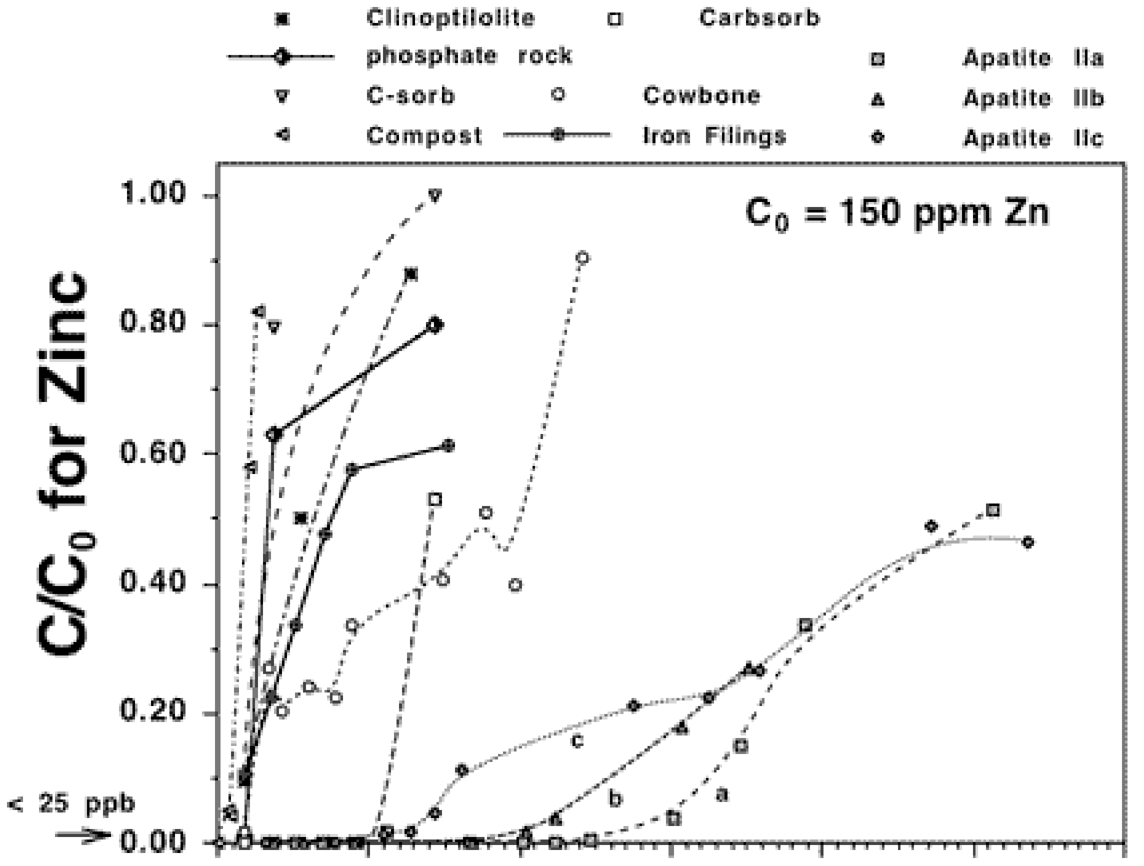

Figure 6. Zn column breakthrough curves for several reactive materials in the feasibility study using groundwater collected from the site.

Of all the media tested, Apatite IIa performed the best with respect to all metals, although all three Apatite II materials performed well. The experiments were stopped for columns that showed rapid breakthrough for Zn. The results for Zn are shown in Figure 6. It should be noted that the compost was run only for its sorption properties. No care was taken to ensure that anaerobic conditions were met that would be appropriate for a reducing bacterial community.

The Zn exhibited rapid breakthrough for the C-sorb, clinoptilolite, iron filings, compost, and even the phosphate rock. Also, the iron filings produced significant colloids that traveled through the column and exited with the effluent. The cow bone apatite showed slightly better performance than iron filings. Carbsorb, which is the zeolite chabazite, acted like an ideal cation exchanger but broke through in a step function after 100 pore volumes. All forms of Apatite II only began to breakthrough after 500 pore volumes. Apatite IIa performed best of all the materials, sequestering about 3% of its weight in Zn during this experiment.

Results for Cd are shown in Figure 7. Most of the materials that exhibited rapid breakthrough for Zn were not run for Cd. The iron filings failed within 24 hours with respect to Cd. The cow bone apatite performed about the same for Cd as for Zn. When the experiments were stopped, Apatite IIc was beginning to show incipient breakthrough with respect to Cd, but the other two Apatite II samples were still below detection for Cd (< 5 ppb Cd).

Based on these results, Apatite IIa was chosen for emplacement in the PRB at the Success site. Extrapolation of the results in Figure 6 indicate that an Apatite II PRB would sequester about 4% to 6% of its weight in Zn, and similarly for Cd. However, Pb is strongly sequestered by apatite and column studies with field concentrations of Pb would take many years to breakthrough. To estimate the loading capacity of Apatite IIa with respect to Pb, a column experiment was run similar to that for Zn, but the

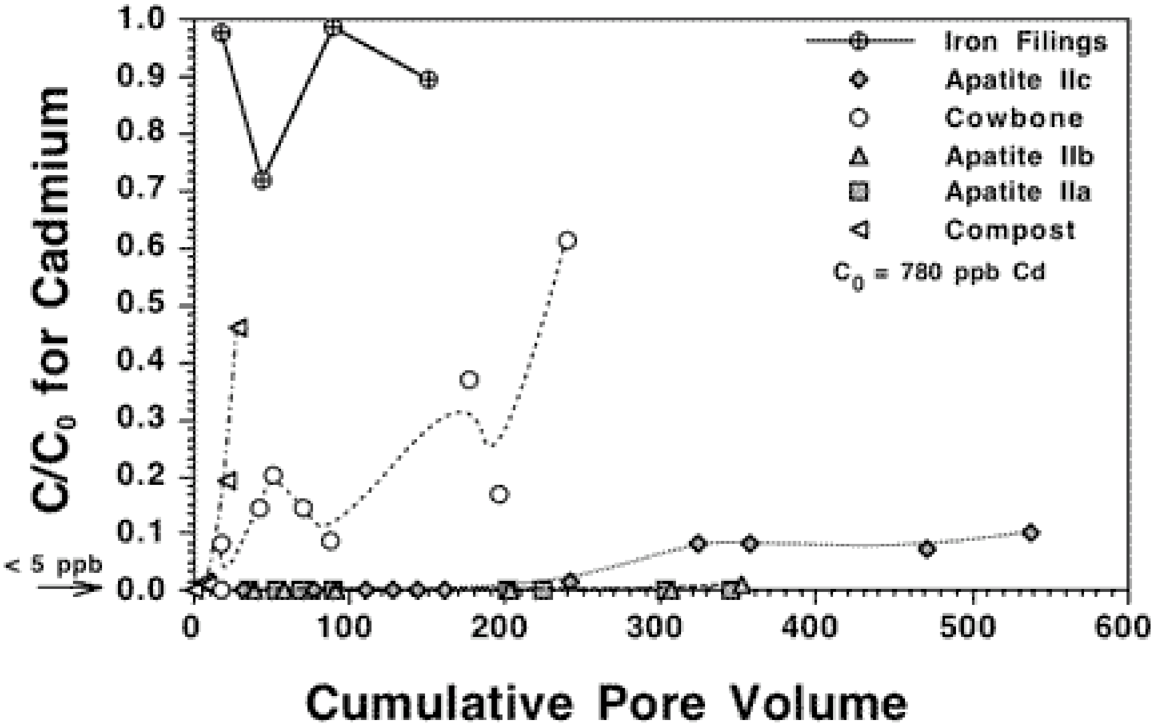

Figure 7. Cd column breakthrough curves for several reactive materials in the feasibility study using groundwater collected from the site.

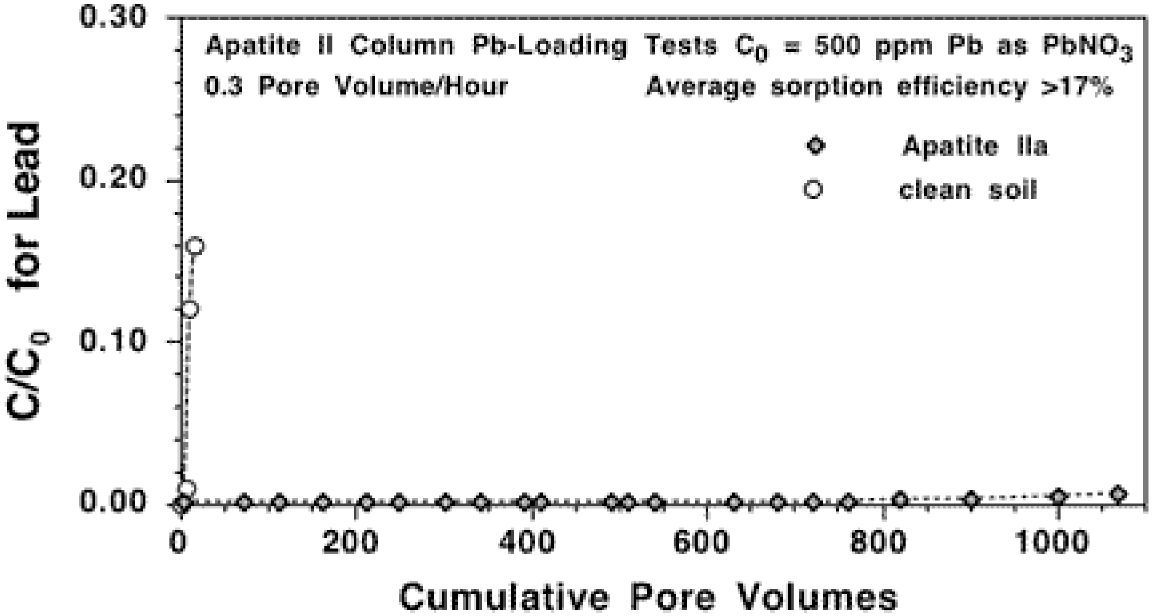

Figure 8. Pb loading experiment for Apatite II. Clean soil is shown for comparison.

influent was spiked with 500 ppm of Pb as $PbNO_3$ in order to induce breakthrough over a shorter time period. The results are shown in Figure 8. Even after 5 months and over 1050 pore volumes at 500 ppm Pb, significant breakthrough did not occur. At this point, the Apatite IIa had sequestered 17% of its weight in Pb. For comparison, clean soil from the site was run and exhibited almost immediate breakthrough.

Reactive media can buffer the pH to varying degrees. Column influent and effluent pH was measured during the column experiments. The influent pH was 4.5 ± 0.3. The pH of the effluents exiting the five apatite columns was between 6.2 and 7.4. The pH of the effluent exiting the C-sorb column was 6.6. The pH of the effluent exiting the compost column was 6.8. The pH of the effluents exiting the zeolite, Carbsorb and iron filings columns was below 5.

FIELD-SCALE PROJECT

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 with grain sizes ranging from clay to boulders up to 5 feet in length. The concentrations of Cd, Pb and Zn within soils and groundwater between the tailings pile and the EFNC are summarized in Tables 2 and 3, along with the EPA's 1999 risk-based guidance levels and water standards. As indicated in Table 3, groundwater quality samples taken from the shallow monitoring wells indicated that the groundwater within the unconsolidated aquifer between the tailings pile and the EFNC significantly exceeds drinking water and aquatic life criteria.

Table 2. Cd, Pb and Zn Levels in soils between the tailings pile and the EFNC

Analyte	*Concentration Range (ppm)*	*Guidance Level (ppm)**
Total cadmium	10.5 - 125	5,700
Total lead	1,690 – 90,800	2,000
Total zinc	1,600 – 9,060	57,000

**EPA risk-based guidance levels in soil under a recreational scenario (less than 8 site visits per year).*

Table 3. Cd, Pb and Zn Levels in groundwater between the tailings and EFNC

Analyte	*Concentration Range (ppb)*	*Drinking Water* Criteria (ppb)*	*Aquatic Criteria† (ppb)*
Dissolved cadmium	8 - 1,250	5	1
Dissolved lead	70 – 1,440	15	2.5
Dissolved zinc	4,850 – 177,000	5,000	100

**Federal Maximum Contaminant Level (MCL) for protection of drinking water.*
†State chronic criteria for the protection of fresh water aquatic life.

Groundwater and surface water level monitoring indicated that surface water flowing within the EFNC recharges the alluvial aquifer over the upper portion of the site. 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 (Figure 5). The hydraulic conductivity of the alluvial aquifer was estimated to range between 1.4×10^{-4} and 4.6×10^{-3} ft/s (with a geometric mean of 1.7×10^{-3} ft/s). This is the hydraulic conductivity characteristic of clean sand and gravel (Freeze and Cherry, 1979). The hydraulic conductivity of the shallow bedrock was estimated to range between 2.0×10^{-5} and 1.5×10^{-4} ft/s (with a geometric mean of 5.6×10^{-5} ft/s). This is the hydraulic conductivity characteristic of fractured igneous rock (Freeze and Cherry, 1979).

Flux estimates based on the site geometry, hydraulic conductivity ranges and water levels measured in May 2000 indicate that between 3 and 101 gpm of shallow groundwater flows out of the alluvial aquifer at the downgradient end of the site. Surface water inflow to the alluvial aquifer over the upper portion of the site is estimated at up to 1,500 gpm based on April 1998 stream gauging (Terragraphics, 1998). Loss of groundwater from the alluvial aquifer to the bedrock at the toe of the tailings pile is estimated to range between 83 to 619 gpm.

PRB Construction

The project goals were: 1) to demonstrate the viability of groundwater collection and treatment; and, 2) to construct a PRB that utilizes materials that performed best during the feasibility study (Apatite IIa) to reduce the concentrations of Cd, Pb and Zn in these waters. Extrapolation of the feasibility results indicated that 100 tons of Apatite IIa could reduce concentrations of dissolved zinc to below 5 mg/L and buffer the pH to above 6 for about three years assuming a flow-through rate of 5 gpm and an inflow dissolved zinc concentration of 155 mg/L. The results indicated that concentrations of dissolved Cd and Pb would also be reduced to below 15 μg/L for many years (UFA Ventures, Inc., 1998). The design concept included construction of a 1,450-foot long pressure-grouted wall between the waste pile and the

EFNC (Golder, 2000b). The wall was designed to extend from the mill foundations at the upper end of the site to a PRB treatment vault sited downgradient of the pile. Vertically, the grout wall was designed to extend within the sub-surface 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. The purpose of the drain is to: 1) direct (under gravity) the groundwater that backs up behind the grout wall towards and through a water treatment facility; and, 2) to minimize the flow of surface water into the shallow groundwater system.

Figure 9. Construction of PRB vault between East Fork of Ninemile Creek and the Tailings Pile in January 2000.

A 13.5-foot high, 15 foot wide by 50 feet long PRB vault with two cells (eastern and western) was poured into rebar forms using Type V (corrosion resistant) Portland cement (Figure 9). The vault was designed with one inflow port, two baffled PRB treatment cells and two outflow ports with a head drop of 7.5 feet from the inflow to the outflow. The plumbing was installed inside the vault and about 108 cubic yards of Apatite II (about 100 tons) were placed within the two cells. 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 allow the inflow to and outflow from the vault to be controlled. The vault outflow discharges to the EFNC via a rock apron outfall. Construction was completed between September 2000 and January 2001 (Figure 10). The cost of the Apatite II was about $350/ton. Emplacement used traditional trenching and earth-moving equipment.

Monitoring

Monitoring was started in January 2001, a few days after the vault valves were opened. Observations were made on the nature of the water flowing into and out of the vault and water levels in front of and within the vault. Field pH and temperature of the water flowing into and out of the vault was measured and the flows out of the vault from the eastern and western discharge pipes were estimated.

Figure 10. Final emplaced Apatite II PRB at Success Mine between East Fork of Ninemile Creek and the Tailings Pile in September 2002.

Water samples were taken at the inflow and outflow and were submitted to an EPA-certified laboratory for analysis of total and dissolved Cd, Pb and Zn. Beginning February 2002, the operation, maintenance and monitoring of the Success PRB was taken over by the Idaho DEQ. The monitoring results to date are presented in Table 4 as an average of the two cells. Generally, the dissolved metal concentrations are greatly reduced and the pH is buffered to between 6 and 7. The reason for the rise in metals concentrations exiting the PRB in June and August 2001 is not entirely clear but may have resulted from hydraulic problems (flooding or circumvention around the PRB cells). Site maintenance activities in September 2001 improved the hydraulic problem and, in October 2001, metals concentrations were again reduced to very low levels.

Although total dissolved phosphorous upstream of the PRB is below 0.04 mg/L, phosphorous loading to the creek from the PRB was found to be between 2 and 20 mg/L total dissolved phosphorous, mostly as orthophosphate, at 5 to 30 gpm. 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 phosphorous) and St Joe at Calder (3 to 10 mg/L total dissolved phosphorous), and is causing no P-loading effects. Based on periodic daily metal-loading averages, it is estimated that the PRB has sequestered over 50 lbs of Cd, over 100 lbs of Pb and over 6,000 lbs of Zn over the two years since it was emplaced. This barrier is estimated to last over thirty years for Cd and Pb, but Zn, which is the contaminant in the highest concentrations, should begin to breakthrough within a few years if the feasibility study results are an

Table 4. Dissolved Metal Concentrations in Groundwater Entering and Exiting the Apatite II PRB

	Entering Barrier (µg/L;ppb)				Exiting Barrier (µg/L;ppb)			
Date	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
3/14/02	4.5	680	1,090	104,000	6.5	< 2	< 5	143

indication of its performance. The barrier has already sequestered over 3% of its weight in metals. Investigation of materials collected from the barrier, detailed geochemistry analyses, and geochemical modeling using MINTEQ and PHREEQ, are ongoing in order to determine which mechanisms are operating in the field and how long the barrier should last. When breakthrough with respect to Zn does occur, either the spent Apatite II can be replaced or a second Apatite II barrier can be emplaced behind the first one, allowing the first one to continue to sequester Cd and Pb and condition the pH while the second captures Zn as it begins to breakthrough the first barrier. If replacement is chosen, the spent Apatite II will almost certainly not be a hazardous waste as spent Apatite II from previous tests passed EPA TCLP tests and could be disposed for less than $20/ton. Alternatively, the spent material can just be left in place after passing leach tests.

CONCLUSIONS

Laboratory feasibility studies demonstrated the greater effectiveness and lower cost of Apatite II relative to other reactive media to treat shallow groundwater containing elevated levels of Pb, Cd and Zn. As a result, 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 Apatite II PRB has been operating at the site since January 2001. 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 emplaced PRB has been operating successfully for over 2 years, and has reduced the concentrations of cadmium (from hundreds of ppb) and lead (from thousands of ppb) generally to below detection (2 µg/L or ppb) and has reduced zinc from almost 100 ppm to near background (about 100 µg/L or ppb) prior to discharge to surface water. During the 2-year operation, the PRB, filled with about 100 tons of

Apatite II (@$350/ton), has removed over 6,000 lbs of Zn, 100 lbs of Pb and 50 lbs of Cd, and has buffered the pH to between 6 and 7. The groundwater PRB treatment system is performing as designed.

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